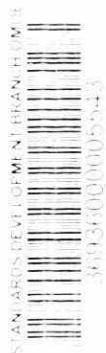


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HAZARDOUS CONTAMINANTS PROGRAMME



ENVIRONMENTAL ASPECTS OF SELECTED
AROMATIC HYDROCARBONS IN ONTARIO:

A COMPREHENSIVE BACKGROUND REPORT

NO. HCP-1-78

September, 1978



Ontario

Ministry
of the
Environment

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ENVIRONMENTAL ASPECTS OF
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A COMPREHENSIVE BACKGROUND

REPORT

NO. HCP-1-78

Prepared For

Air Resources Branch
Ontario Ministry of the Environment

By

United Technology and Science Inc.

September, 1978

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I TABLE OF CONTENTS



TABLE OF CONTENTS

SECTION		PAGE NO.
1	TABLE OF CONTENTS	1-1
2	LIST OF TABLES	2-1
3	LIST OF FIGURES	3-1
4	SUMMARY	4-1
5	CONTRACTOR'S WORK PROGRAM	5-1
6	INTRODUCTION	6-1
7	CHEMICAL AND PHYSICAL PROPERTIES OF AROMATIC HYDROCARBONS	7-1
7.1	Summary	7-4
7.2	Introduction	7-5
7.3	Benzene	7-8
7.4	Toluene	7-26
7.5	Xylenes and Ethylbenzene	7-44
7.6	Cumene	7-62
7.7	Styrene	7-69
7.8	Naphthalene	7-75
7.9	References	7-88
8	MAJOR PRODUCERS, USES AND MARKET FORECASTS	8-1
8.1	Summary	8-4
8.2	Introduction	8-11
8.3	Benzene	8-12
8.4	Toluene	8-34



SECTION		PAGE NO.
8.5	Xylenes and Ethylbenzene	8-50
8.6	Styrene	8-63
8.7	Cumene	8-79
8.8	Naphthalene	8-84
8.9	References	8-88
9	PROCESS DESCRIPTIONS	9-1
9.1	Introduction	9-4
9.2	Production of Benzene, Toluene and Xylene (BTX)	9-6
9.3	Production of Ethylbenzene	9-20
9.4	Production of Styrene	9-24
9.5	Styrene Polymerization	9-29
9.6	Production of Phthalic Anhydride	9-42
9.7	Coking	9-50
9.8	Coal Tar Distillation	9-57
9.9	References	9-59
10	EMISSION AND DISCHARGE CONTROL TECHNOLOGY	10-1
10.1	Summary	10-3
10.2	Air Emission Control	10-8
10.3	Waste Water Effluent Control	10-44
10.4	Waste Disposal Methods	10-90
10.5	References	10-97
11	SAMPLING AND ANALYSIS	11-1
11.1	Summary	11-3
11.2	Introduction	11-4
11.3	Sampling and Analysis of Aromatic Hydrocarbons in Occupational Atmospheres	11-6
11.4	Sampling and Analysis of Aromatic Hydrocarbons in Ambient Air	11-17



SECTION		PAGE NO.
11.5	Sampling and Analysis of Aromatic Hydrocarbons as Water Pollutants	11-34
11.6	References	11-39
12	ENVIRONMENTAL PERSISTENCE AND FATE	12-1
12.1	Summary	12-3
12.2	Introduction	12-8
12.3	Aromatic Compounds in Air	12-10
12.4	Aromatic Compounds in Water	12-52
12.5	References	12-66
13	HEALTH EFFECTS	13-1
13.1	Introduction	13-7
13.2	Benzene	13-10
13.3	Toluene	13-47
13.4	Xylene	13-73
13.5	Naphthalene	13-90
13.6	Cumene	13-94
13.7	Styrene	13-97
13.8	Ethylbenzene	13-114
13.9	References	13-116
14	STANDARDS	14-1
14.1	Summary	14-3
14.2	Occupational Health Standards	14-5
14.3	Ambient Air Standards	14-10
14.4	Water Standards	14-12
14.5	References	14-13



2 LIST OF TABLES



LIST OF TABLES

TABLE		PAGE NO.
	<u>SECTION 7</u>	
7-1	Physical Properties of Benzene	7-11
7-2	Vapor Pressure-Temperature Relationship for Benzene	7-14
7-3	Physical and Thermodynamic Properties of Toluene	7-27
7-4	Azeotropes of Toluene	7-29
7-5	Vapor Pressure-Temperature Relationship for Toluene	7-31
7-6	Physical and Thermodynamic Properties of the Eight Carbon Atom Aromatic Isomers	7-46
7-7	Activity Coefficient of C ₈ Aromatic Isomers	7-49
7-8	Vapor Pressures of C ₈ Aromatics	7-50
7-9	Physical and Thermodynamic Properties of Cumene	7-63
7-10	Vapor Pressure-Temperature Relationship for Cumene	7-65
7-11	Physical Properties of Styrene	7-70
7-12	Vapor Pressure-Temperature Relationship for Styrene	7-73
7-13	Physical Properties of Naphthalene	7-78
7-14	Vapor Pressure- Temperature Relationship for Naphthalene	7-79
7-15	Binary Azeotropes for Naphthalene	7-80
	<u>SECTION 8</u>	
8-1	Companies Producing Benzene from Petroleum in Canada and Total Plant Capacities, 1975 and 1977	8-15
8-2	Estimates of Benzene Supply and Demand 1974-76 and Forecasts for 1977	8-16



TABLE	PAGE NO.
8-3 Amounts of Coke and Benzene Produced in Canada and Ontario, 1974-77 from Coal Carbonization	8-20
8-4 Benzene Content of Gasoline Blending Components at Two U.S. Refineries	8-23
8-5 Aromatics Content of Refinery Streams used for Gasoline Blending in an Ontario Refinery	8-24
8-6 Estimated End-Use Pattern for Benzene Produced in Canada in 1977	8-27
8-7 Consumption of Benzene by Industry	8-29
8-8 Forecast for Benzene Supply and Demand in Canada to 1990	8-31
8-9 Canadian Producers of Toluene and Estimates of Production Capacity for 1975 and 1977	8-38
8-10 Amounts of Coke and Toluene Produced in Canada and Ontario 1974-77 from Coal Carbonization Operations	8-40
8-11 Estimated End-Use Pattern for Toluene Produced in Canada in 1976	8-44
8-12 Amounts of Toluene Used by Canadian Industries (1973-75) and Total Amounts Shipped and Imported	8-47
8-13 Average Composition of Mixed Xylenes from Extracted Reformate	8-52
8-14 Companies Producing Xylenes from Petroleum in Canada and Total Plant Capacities, 1975 and 1977	8-54
8-15 Amounts of Xylenes Shipped, Imported and Consumed by Industry	8-59
8-16 Estimated End-Use Pattern for Styrene in Canada (1977)	8-67
8-17 Polystyrene Market Breakdown	8-68
8-18 Styrene-Butadiene Rubber Market Breakdown	8-69
8-19 Styrene-Butadiene Latex Market Breakdown	8-70
8-20 Acrylonitrile-Butadiene-Styrene Terpolymer/ Styrene-Acrylonitrile Copolymer (ABS/SAN) Market Breakdown	8-71



TABLE		PAGE NO.
8-21	Canadian Producers of Styrene Derivatives	8-73
8-22	Amounts of Styrene Used by Various Industries and Total Amounts of Styrene Consumed 1973-1976	8-74
8-23	Supply/Demand Forecasts for Styrene and Major Derivatives	8-77

SECTION 9

9-1	Analysis of Typical Pyrolysis Gasoline	9-9
9-2	Characteristics of Wastewater from Two-Stage Hydrotreating of Pyrolysis Gasoline	9-12
9-3	Aromatic Extraction Feedstock Composition	9-13
9-4	Aromatics Separation Feedstock	9-16
9-5	Ortho-Xylene Separation Feedstock Composition	9-18
9-6	Stream Code for BASF Process Illustrated in Figure 9-8	9-46
9-7	Emission Factors for Phthalic Anhydride Plant o-Xylene Based - Production 5.9×10^4 Metric Tons/Yr. Scrubber-Incinerator Control	9-48
9-8	Estimated Emissions for a 45 Gg/Yr Phthalic Anhydride Plant Scrubber-Incinerator Control	9-49
9-9	Emission Factors for Metallurgical Coke Manufacture Without Controls	9-54
9-10	Potential Total Emissions from Ontario Metallurgical Coke Manufacturers	9-55
9-11	Average Analysis of Quench Water Samples	9-56

SECTION 10

10-1	Solubility of Organic Compounds in Water at 25 °C	10-46
10-2	Toxicity of Aromatic Compounds to Fish	10-47
10-3	Influence of Molecular Structure and Other Factors on Adsorbability	10-72



TABLE	SECTION 12	PAGE NO.
12-1	Reactivity Scale for Organics Based on Rate of Consumption Due to Reaction with the Hydroxyl Radical	12-27
12-2	Reactivity Classification Based on Reaction with the Hydroxyl Radical	12-28
12-3	Reactivity Classification Based on Hydrocarbon Consumption - I	12-30
12-4	Reactivity Classification Based on Hydrocarbon Consumption - II	12-31
12-5	Relative Reactivities of Hydrocarbons Based on Ability to Participate in Photooxidation of Nitric Oxide to Nitrogen Dioxide	12-33
12-6	Reactivities of Aromatics, Paraffins and Olefins Based on NO Oxidation	12-34
12-7	Hydrocarbon Reactivity Classification Based on Maximum O ₃ Production - I	12-37
12-8	Hydrocarbon Reactivity Classification Based on Maximum O ₃ Production - II	12-39
12-9	Hydrocarbon Reactivities Based on O ₃ Formation	12-40
12-10	Reactivity Classification for Various Hydrocarbons Based on Average Ozone Concentrations Up to 99 % of Hydrocarbon Decomposition	12-42
12-11	Reactivity Parameters for Various Hydrocarbons	12-43
12-12	Eye Irritation Reactivity	12-46
12-13	Average Measured Concentrations of Aromatic Compounds in Ambient Air in Cities	12-50
12-14	Calculated Evaporative Half Lives of Aromatics in Water Bodies at 25 °C	12-54
12-15	Quantitative Analysis of Aromatic Hydrocarbons in Plant Effluents	12-59
12-16	Organic Compounds Identified in St. Clair River Sediments	12-60
12-17	Trace Organics Apart from Haloforms Identified in Drinking Water Supplies	12-61
12-18	Aromatic Hydrocarbons Identified at Cayuga Water Treatment Plant	12-62



TABLE

PAGE NO.

12-19	Aromatics in Water and Sediment Near a Specialty Chemical Plant	12-65
-------	--	-------

SECTION 14

14-1	Current or Proposed Occupational Standards for Aromatic Hydrocarbons in North America	14-7
14-2	Threshold Limit Values for Aromatic Hydrocarbons in Sweden and Germany	14-9
14-3	Half-Hour Point-of-Impingement Standards for Aromatic Hydrocarbons in Ontario	14-11



3 LIST OF FIGURES



LIST OF FIGURES

FIGURE		PAGE NO.
<u>SECTION 8</u>		
8-1	Uses of Benzene and Derivatives	8-26
8-2	Uses of Toluene and Derivatives in North America	8-43
8-3	Uses of Xylenes and Derivatives	8-57
8-4	Uses of Phthalic Anhydride and Derivatives	8-58
8-5	Uses of Styrene and Derivatives	8-66
8-6	Uses of Cumene and Cumene Derivatives	8-81
8-7	Uses of Phenol and Derivatives	8-82
8-8	Uses of Naphthalene and Naphthalene Derivatives	8-87
<u>SECTION 9</u>		
9-1	Flow Chart of BTX Production Processes	9-7
9-2	Ethylbenzene Manufacture Employing Aluminum Chloride as Catalyst	9-21
9-3	Styrene Manufacture by Adiabatic Dehydrogenation of Ethylbenzene	9-25
9-4	Continuous Solvent Process for Styrene Polymerization	9-30
9-5	Styrene-Butadiene Manufacture	9-34
9-6	Flow Chart for ABS Manufacture	9-38
9-7	Manufacturing Process for Unsaturated Polyesters	9-41
9-8	BASF Process for Manufacture of Phthalic Anhydride from o-Xylene	9-45
<u>SECTION 10</u>		
10-1	Hydrocarbon Control System - Condensation	10-10
10-2	Relationship Between Pore Size and Vapor Concentration	10-16



FIGURE		PAGE NO.
10-3	Adsorption Isotherms for Solvents on Activated Carbon	10-17
10-4	Adsorption Isotherms of Benzene on Activated Coconut Charcoal at Atmospheric Pressure	10-18
10-5	Formation and Movement of the MTZ Through an Absorbent Bed	10-20
10-6	Benzene Adsorption Isobar on Carbon	10-24
10-7	Two-Unit Fixed-Bed Adsorber	10-27
10-8	Verticle Adsorber with Two Cones (permitting Studies on Different Depths of Carbon Beds)	10-29
10-9	Direct Flame Thermal Incinerator	10-33
10-10	Hydrocarbon Oxidation Rates in Absence of Flame	10-35
10-11	API Oil Water Separator	10-50
10-12	Dissolved Air Flotation	10-52
10-13	High Rate Sand Filtration	10-53
10-14	Basic Wet Air Oxidation Flow Scheme	10-56
10-15	Wet Air Oxidation - Biophysical Treatment	10-57
10-16	Microbial Oxidation of Aromatic Compounds	10-60
10-17	Extraction System	10-63
10-18	Activated Sludge Treatment	10-68
10-19	Fruendlich Isotherm Application	10-76
10-20	Schematic of Pilot Plant for Carbon Adsorption Testing	10-77
10-21	Ideal Breakthrough Curve for Activated Carbon	10-79
10-22	COD Breakthrough Curve	10-80
10-23	Schematic of Carbon Regeneration System	10-81
10-24	Flow Diagram of Biophysical Treatment	10-83
10-25	Candidate System Application for Carbon Columns within a Refinery Treatment Complex	10-85
10-26	Removal of Chlorinated Hydrocarbon by Catalyzed-Iron Reducing Agent	10-88



FIGURE

PAGE NO.

SECTION 11

11-1	Breakthrough Volumes for Benzene and Toluene on Tenax GC Over a Range of Ambient Temperatures	11-23
------	---	-------

SECTION 12

12-1	Concentration Changes on Irradiation of a Mixture of ($\text{NO} + \text{NO}_2 + \text{C}_3\text{H}_6$)	12-13
------	--	-------



4 SUMMARY



SUMMARY

The light aromatic compounds considered in this report are: benzene, toluene, xylene, ethylbenzene, cumene, styrene, naphthalene.

Chemical and Physical Properties

With the exception of naphthalene, all of these compounds are noncorrosive, clear, colorless, refractive, volatile liquids at standard temperature and pressure. These liquids are highly flammable and burn with a sooty flame. Naphthalene is a solid and is easily sublimed. It has a mild characteristic odor. The other compounds have pungent odors characteristic to this class of compounds.

Benzene is the most soluble in water among these compounds ($\sim 2 \text{ g l}^{-1}$). Solubility in water ranges from $\sim 2 \text{ g l}^{-1}$ for benzene to $\sim 0.04 \text{ g l}^{-1}$ for cumene. In addition, most of these compounds are miscible with the common organic solvents.

The unique properties of aromatic hydrocarbons are derived from the stability of the six carbon-atom benzene ring structure, or aromatic nucleus, which is the basic structural unit of these compounds. There are small differences due to substituent alkyl groups, however, the major chemical properties are similar.

The main types of chemical reactions in which these compounds take part are substitution, addition, and cleavage of the aromatic ring.

Alkyl substituted aromatics can undergo disproportionation and transalkylation reactions with each other. These reactions are usually reversible.

In addition to the reactions mentioned above, styrene can be polymerized and undergoes all of the normal reactions of a typical unsaturated compound such as addition across the double bond, etc.



Major Producers, Uses, and Market Forecasts

The major producers of these compounds are the petroleum refineries and the petrochemical industry. Small amounts are also produced from coking operations. In Canada, all production of isolated naphthalene is from feedstocks produced by the coke industry.

Production figures for these compounds generally refer to production of the isolated compound. However, it must be remembered that large quantities of mixed aromatic compounds (produced in petroleum refinery streams) are blended directly into gasoline pools without prior separation.

Most of the benzene production in Ontario is located in the Sarnia area. In 1977, capacity was about 200 Gg/annum (50 % of Canadian production). In 1978, this is expected to rise to 470 Gg/annum (70 % of Canadian production). Capacity is expected to increase (from 1977 to 1990) by 75 % with an average annual increase in demand of 8.5 % from 1976 to 1990. In addition, it is estimated that about 110 Gg of benzene was present in gasoline used in Ontario during 1977, based on available statistical data indicating sales of 12.7 GL of gasoline for road use.

The major use of benzene in Canada is in the petrochemical industry. In Ontario, almost all of the benzene is used in reaction with ethylene to produce styrene for plastics manufacture. No cumene, or maleic anhydride are produced in Ontario. Almost 50 % of Canadian benzene production is exported.

Toluene production in Ontario is also located mainly in the Sarnia area with a 1977 capacity of 200 Gg/annum (55 % of Canadian capacity). By the end of 1978 this should reach 340 Gg/annum (70 % of Canadian capacity).



In Canada (1977), it is estimated that approximately 25 % of the toluene produced was returned back into gasoline blending streams, 20 % was used to produce benzene, 6 % for phenol production, 10 % for solvents, 5 % for miscellaneous uses, and 34 % exported. No benzene or phenol are produced in Ontario from toluene. It is estimated that about 660 Gg/annum of toluene were present in gasoline used in Ontario in 1977.

In Ontario, most of the xylene production is located in the Sarnia area from petroleum refinery streams. The 1977 Ontario capacity was 250 Gg/annum (45 % of Canadian capacity). No isolation of isomers is presently carried out in Ontario. However, about 12 Gg/annum of o-xylene are used in Ontario to produce phthalic anhydride.

It is estimated that 90 % of the xylene produced in Ontario is blended back into gasoline streams and that about 1,100 Gg of xylene was present in gasoline used in Ontario in 1977.

Ethylbenzene is produced in Ontario in Sarnia by the reaction of benzene with ethylene. The current capacity is about 200 Gg/annum and this is all used to produce styrene for polymer production. It is not known how much ethylbenzene is present in gasoline.

Styrene production capacity in Ontario for 1977 is about 200 Gg/annum. Styrene is estimated to be present at about 0.5 % in gasoline. This corresponds to about 60 Gg used in 1977 in Ontario for that purpose. It is estimated that demand for styrene will grow at an average annual rate of 7 % from 1976 to 1990.

Naphthalene production in Ontario is from coke industry product streams in Hamilton and Sault Ste. Marie. The 1976 production capacity was 20 Gg/annum (80 % of Canadian capacity) with 15 Gg exported for



phthalic anhydride manufacture and the remainder used for miscellaneous chemical manufacture. The concentration of naphthalene in gasoline is not known but could range up to 1 % which would correspond to about 120 Gg used in Ontario during 1977.

No cumene is produced or used in Ontario.

Process Descriptions

The majority of benzene, toluene and xylene (BTX) is produced in petroleum refineries with aromatic units. Some aromatics are produced in coking operations (light oils) and these are shipped to refineries for addition to their operating streams. The petroleum feedstock for BTX production is either catalytic reformat (reformed naphthenes) or pyrolysis gasoline (a by-product of olefin production by thermal cracking).

Pyrolysis gasoline is first treated in a hydrotreating unit which saturates the diolefins and mono-olefins to produce a stabilized mixed aromatics stream. Sulfur and nitrogen compounds are converted to H_2S and NH_3 which are removed. The stabilized output from the hydrotreating unit and/or catalytic reformat are then fed to the aromatic extraction unit. This is a solvent extraction process - either the UDEX process or the sulfolane process. UDEX extraction uses di-, tri-, or tetra-ethylene glycol/water mixtures while the sulfolane uses tetrahydrothiophenedioxide. In both systems the product is a mixed aromatic extract and raffinate, which contains mainly paraffins. Benzene, toluene and the mixed xylenes (C_{8+} aromatics) are separated by distillation.

Most of the ethylbenzene production in Ontario is based on the "Friedel-Craft" alkylation of benzene by ethylene. Almost all of this ethylbenzene



is then converted to styrene by dehydrogenation.

Styrene is used extensively as a monomer in the production of a number of plastics. Polystyrene is produced either by the suspension or the bulk continuous process. Styrene-butadiene rubber (SBR) is produced using styrene and butadiene monomers in the cold or hot emulsion process. Styrene-acrylonitrile polymers (SAN) are produced by mass polymerization in a batch process using mixtures of both monomers. In the production of acrylonitrile-butadiene-styrene (ABS) polymers, a polybutadiene latex is mixed and reacted with monomer styrene and acrylonitrile. Styrene is also used for cross linking in the production of unsaturated polyesters by adding the styrene monomer to prepolymer unsaturated polyester.

The major use of o-xylene in Ontario is for the production of phthalic anhydride by the BASF o-xylene oxidation process.

Coking operations involve the pyrolysis of coal in the absence of oxygen. In addition to coke, light oils and coal tars are produced. Light oils are shipped to refineries. Coal tars are separated into various products (including naphthalene) by distillation.

Emission and Discharge Control Technology

Air emission control systems are usually an integral part of manufacturing technology. As a consequence, process data are considered proprietary, and are not usually available to the public. Condensation, absorption, adsorption and incineration are the most frequently used control systems. A multistage condensation system with refrigeration in the final stage can achieve a 99+ % removal efficiency for the compounds of interest here. Water,



mineral oils, non-volatile hydrocarbon oils and various aqueous solutions are used for the absorption of hydrocarbons. Absorption systems can be designed to achieve up to 95 % removal efficiency. Adsorption on the surface of specially prepared granular solids, and adsorbents, is a very efficient method for selective removal of hydrocarbons from gaseous streams. Activated charcoal is the most widely used adsorbent. Incineration is frequently used in the petrochemical industry. A retention time of 2 seconds at 1000 °C is considered satisfactory for the destruction of most organics. Flares are not considered as environmentally satisfactory for the disposal of hazardous gases because of incomplete combustion and noise pollution problems.

A major source of hydrocarbon losses is during storage and transfer operations. The use of floating roofs, vapor recovery units and reduction of fugitive emissions (pump seals, relief valves, etc.) could considerably reduce these losses.

Removal of hydrocarbons from water discharges requires several steps and includes primary nonsolubilized hydrocarbon removal followed by solubilized hydrocarbon removal. Biological oxidation is used, although for aromatic hydrocarbons it is a slow process. A complete removal of hydrocarbons from waste water effluents can be achieved by:

- primary treatment such as gravity oil-water separation and, induced air flotation (IAF), dissolved air flotation (DAF) or filtration followed by
- the series: biological oxidation - carbon adsorption treatment or



- the series: carbon adsorption - biological oxidation treatment or
- carbon adsorption as the only treatment

Other available technologies are steam stripping, solvent extraction, membrane processes and wet air oxidation.

Waste disposal by incineration is an ultimate disposal method if properly designed and operated. A residence time of 2 seconds at 1000 °C is considered adequate for most organic compounds. Incomplete combustion of chlorinated compounds may result in emissions of phosgene and hydrogen chloride. Excess hydrogen is required to form HCl which can be recovered. Deep wells and land fill sites have often been used in the past but sites are becoming more and more difficult to find where there is no risk of ground water contamination.

Sampling and Analysis

Occupational atmospheres have been sampled for these compounds using various methods such as grab samples in plastic bags or other containers, absorption in impingers by nitrating solutions or organic solvents and adsorption on such sorbants as silica gel or activated charcoal. Analytical methods include such techniques as colorimetry, infrared and ultraviolet spectroscopy and gas chromatography. The most widely accepted method in North America (recommended by NIOSH and OSHA) is sampling by adsorption on activated charcoal, followed by desorption with carbon disulfide and analysis by gas chromatography (GC).

Ambient atmospheres are more difficult to sample and analyse due



to the low concentrations of the compounds of interest and because of the large number of other compounds frequently present in admixture. Many sampling methods have been used such as grab sampling in plastic, glass, or stainless steel containers. Enrichment methods such as condensation, absorption and adsorption have been used. The best technique, at the present time, appears to be adsorption on Tenax GC followed by thermal desorption into a GC equipped with a mass spectrometer for compound identification. It appears that glass support-coated capillary columns have the best resolving power currently available.

Methods of sampling water for aromatic hydrocarbons have included solvent extraction, activated carbon adsorption followed by solvent extraction, head space analysis and inert gas stripping. The most widely accepted method of analysis is gas chromatography.

Environmental Persistence and Fate

The major degradation pathway for the compounds of interest here is probably atmospheric photooxidation - regardless of the media in which the primary emissions occur. Studies have shown that evaporative half lives of these compounds from aqueous discharges is relatively short (less than about seven hours for the longest case). With the possible exception of naphthalene, there does not appear to be any significant accumulation of these compounds in sediments. Although biological degradation of these aromatic compounds can take place, it is a slow process and does not compete with evaporation. Also, with the possible exception of styrene, hydrolysis and aqueous oxidation do not take place at a significant rate.



Atmospheric degradation of aromatic compounds takes place via photooxidation in the well known photochemical smogs. However, details of reaction mechanisms and products for aromatic compounds are not well understood. These compounds have not been included in simulation models of photochemical smog to date due to the lack of information about their reactive mechanisms. Some smog chamber studies have been carried out using these compounds, and they are known to produce aerosols. However, as they are slow reacting, long experiments (longer than eight hours) are required and this is difficult to carry out due to wall effects and trace impurities.

General reactivity scales have been proposed for these compounds based on various criteria. The relative ordering of increasing reactivity is:

- benzene
- naphthalene
- toluene
- ethylbenzene
- cumene
- xylene
- styrene

It has been found in photochemical smogs that styrene and alkylbenzenes are precursors to the formation of the potent eye irritant peroxybenzoylnitrate (PBN).

There are very few reported ambient measurements of aromatics. In Toronto, hourly averages of ambient air levels of benzene and toluene have been reported as an average of 13 and 30 ppb respectively, with a maximum of 98 and 188 ppb. These levels were associated with automobile



traffic. Actual concentrations observed vary widely with site and time of day. Reports for a number of urban and industrial areas indicate that hourly average concentrations for benzene, toluene, ethylbenzene, and the xylenes range from about 3 ppb up to 50 ppb.

These compounds are generally not detectable in aqueous samples except at industrial effluent outflow sites where concentrations may reach several hundred ppm. They are, however, rapidly lost downstream from the source.

There have been some cases where aromatics were found at the ppt level in finished drinking waters in Ontario. The source was attributed to contamination of the anthracite filter medium caused by occasional relatively higher levels of aromatics in the raw water entering the treatment plant.

Health Effects

The following is a brief summary of biological information for each compound of interest. Included is a three category toxicity rating (A, B and C) for each compound. The selection of such a cryptic rating system contains a considerable degree of subjective judgement. It is important to keep in mind that the data upon which the categories are based are very seldom complete and/or are often not of a uniformly high quality. Due to this, and a number of other qualifying factors (described in detail in Section 13), undue precision and authority should not be drawn from the category scheme.

Note also that the biological rating system refers only to toxicity



which is the ability to cause harm after reaching the target organ or organism. The more important factor upon which to base policy and administrative decisions is related to the hazard to health that a chemical poses. Hazard is an expression of the probability that a chemical will reach the target organ or organism in sufficient quantity to cause harm. Hazard must take into account such factors as the spatial and temporal relationships between the emissions, and the receptor, transport factors, numbers of receptors, etc.

Of the three letters used for ranking, A represents the highest toxicity and C the lowest.

Benzene

At low levels, irritating to nose and eyes, narcotic at higher levels, can cause aplastic anemia and there is some epidemiological evidence that it may cause leukemia in man. Data are inadequate to establish dose-response relationships at concentrations of benzene found in ambient air.

Toxicity Rating: [A]

Low acute toxicity but given [A] rating because chronic exposure may lead to aplastic anemia and/or leukemia.

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low (produces narcosis)
Chronic	High (depression of bone marrow)

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	Not relevant in view of epidemiological evidence



Epidemiological

(high) [A] (carcinogen)

Toluene

Irritant to nose and eyes at about 200 ppm. Onset of "drunkenness" (central nervous system depression) at about 400 ppm. Irreversible effects not reported in range of average present occupational exposures (up to 100 ppm); toluene in early studies often contaminated with benzene. Odor threshold 4-5 ppm.

Toxicity Rating: [C]

No evidence of chronic effects at levels up to 100 ppm TWA in occupational exposure. There are no reports, at present, suggesting that lifetime exposure at the levels of toluene currently encountered in the ambient environment would exert a harmful effect on health. As with any such statement it may require modification in the light of new knowledge. In particular, the possibility of synergistic effects of toluene with other agents having an effect on the central nervous system should be recognized and information on such effects should be sought.

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	Low

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	Low
Epidemiological	Low



Xylene

Irritant to nose and eyes at levels about 200 ppm. Onset of narcotic (central nervous system depression) effects at about 200 ppm. Irreversible effects not reported at average present occupational levels (up to 100 ppm). Odor threshold about 1 ppm. Odor may cause complaints close to source.

Toxicity Rating: [C]

No irreversible effects at levels below 100 ppm in occupational exposure (40 hour week).

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	Low

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	Low
Epidemiological	Low

Naphthalene

Eye and skin irritant. Lens opacity reported in 8 of 21 persons exposed to "high" levels. Cataracts found in rabbits dosed at "high" levels. No chronic effects reported at present levels of occupational exposure (average up to 10 ppm). At levels above 10 ppm, inhalation may cause headaches. Ingestion of high levels (moth balls) in children has caused hemolytic anemia.



Toxicity Rating: [B]

Data are scanty, acute toxicity appears low. Some suggestion of chronic effects on eyes and blood but recovery after ending exposure, exposure levels causing effects were probably "high".

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	Moderate

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	No Data
Epidemiological	Moderate (little data)

Cumene

Skin irritant and central nervous system depressant. No human poisoning reported. Acute toxicity higher than benzene and toluene. Slow elimination from animals suggests possibility of cumulative effects.

Toxicity Rating: [C]

Rating [C] occupational exposure limit 50 ppm (TWA).

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Moderate
Chronic	No Data

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	No Data
Epidemiological	No Data



Styrene

Skin and eye irritant, changes in EEG reported at average exposure of 30 ppm. Central nervous system depressant. Some reduction in pulmonary function in chronically exposed workers, styrene shown to be mutagenic and therefore a suspected carcinogen. Odor threshold is 0.1 ppm. Occupational exposure limit TWA 100 ppm.

Toxicity Rating: [A]

Given rating of [A] on basis of suspected carcinogen due to mutagenicity. No human studies confirm carcinogenicity, but no long term studies are reported. At low concentrations odor produces complaints.

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	Moderate

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	Moderate
Epidemiological	Moderate

Ethylbenzene

Skin irritant and central nervous system depressant. Very few data are available but no evidence of chronic effects from occupational exposure. Occupational exposure limit TWA 100 ppm.

Toxicity Rating: [C]Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	No Data



Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	No Data
Epidemiological	No Data

Standards

In Ontario the occupational standards for the aromatic compounds of interest here are based on eight hour average concentrations and are the same as the TLVs recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). Current standards are listed as:

- benzene	10 (32) ppm (mg.m^{-3})
- toluene	100 (375)
- xylene (o-,m-,p-)	100 (375)
- ethylbenzene	100 (375)
- cumene	50 (245)
- styrene	100 (420)
- naphthalene	10 (50)

The Ontario standards are identical to the recommended TLVs of the ACGIH and, with the exception of benzene, to TWAs set by OSHA in the U.S. In the U.S. the TWA for benzene is currently 1 ppm or 3 mg.m^{-3} with a ceiling of 5 ppm or 16 mg.m^{-3} . Enforcement of this lower level for benzene has been temporarily restrained pending the outcome of a federal appeal court decision.



In Ontario, ambient air standards, which refer to a half hour average point of impingement concentration, have been promulgated for most of the compounds of interest here. The regulations are:

- benzene	10.0 mg.m ⁻³
- toluene	2.0
- xylenes	2.3
- ethylbenzene	4.0
- styrene	0.40

Water quality standards currently in force generally use such parameters as: COD, BOD, TOC, turbidity, fish toxicity, etc. No standards specific for the aromatic compounds of interest here were found.



5 CONTRACTOR'S WORK PROGRAM



5

CONTRACTOR'S WORK PROGRAM

An exact copy of the contractor's work program which sets the scope for the study leading to this report and its companion report entitled "Environmental Aspects of Selected Chlorinated Hydrocarbons in Ontario: A Comprehensive Background Report" is reproduced on the following pages. During the execution of the study a few, relatively minor changes in the work program were agreed upon between UNITED TECHNOLOGY and SCIENCE INC. and the Ministry project officer. These changes are reflected in the content of the reports.

Recommendations arising from this study are contained in a separate report to the Ministry of the Environment.



SCHEDULE ONEContractor's Work Programme

The Contractor will undertake to provide the Ministry of the Environment with two(2) comprehensive reports- one report each for selected chlorinated hydrocarbons, and for selected aromatic hydrocarbons. These in-depth reports are to cover all aspects which are relevant to the role of these compounds as environmental pollutants in Ontario. Each report should represent a state-of-the-art summary and review of up-to-date scientific, technical and medical information. The information will be obtained by means of literature searches and from a reading of current literature, and be supplemented as required by discussions with knowledgeable professional staff in the university, government and industrial communities. The information and data must be as current as reasonable access to scientific governmental, and industrial sources allows, and should be the most reliable information that is available. Although the Contractor is not expected to reconcile conflicting data, he should endeavour to provide some evaluation and synthesis of the collected information. The Contractor is not expected to generate new laboratory data, or engage in environmental surveys or source testing programmes.

These comprehensive reports should be prepared in sufficient detail to serve as a basis for Ministry policy determination and abatement program design, and otherwise sound decision-making on future Ministry activities.

The study will start with a specification by the Ministry of the Environment of a group of substances which belong to the



chlorinated hydrocarbon and aromatic hydrocarbon classes of chemicals. A preliminary list of compounds is as follows:

Chlorinated Hydrocarbons:

- Ethylene Dichloride
- Carbon Tetrachloride
- Vinylidene Chloride
- Tetrachloroethylene
- Methyl Chloride
- Chloroprene
- Chloroform
- Methylene Chloride
- Dichloroethylene
- Trichloroethylene
- Trichloroethane

Aromatic Hydrocarbons:

- Benzene
- Toluene
- Xylenes
- Naphthalene
- Cumene
- Styrene
- Ethyl Benzene

The study will be carried out in two stages.

Stage 1

The Contractor will carry out activities to identify the potential sources of environmental emissions for each compound contained in the list specified by the Ministry. Specifically the Contractor and the final report must give consideration to the following points:

Potential Sources of Environmental Emissions

- (a) Types of industries in Ontario which use or produce the specified compounds. Identification of processes and products.
- (b) Estimates of total quantities used or produced in Ontario.

Quantities to be subdivided into categories by industrial products, applications, etc.



- (c) Description of major industrial operations and processes which are potential sources. Identification of sources of emissions and types of pollutants.
- (d) Description of potential secondary emitters such as incinerators, non-industrial sources, and ubiquitous sources.
- (e) Estimates of potential environmental emissions or discharges specific to Ontario industries, derived from a knowledge of the industrial operations, control equipment in use, and/or published values of source strengths or emission factors.
- (f) Assessment of the population size potentially exposed to the specified compounds, to be carried out by means of product application assessments and the location of major emitters.

The data collected on industrial sources together with preliminary information on specific health hazards of these compounds will be used in a priority determination to select the compounds for the more intensive information gathering of Stage 2 of this study. This selection will be carried out in consultation with Ministry staff. It is expected that most of the compounds presented above will be considered in Stage 2 since this list already reflects assessments of priority compounds by Ministry staff.

The Contractor will prepare a written progress report at the conclusion of Stage 1 of this study. This progress report is to be in sufficient detail that Ministry staff will be able to identify the major industries, processes, and operations, which use or produce the specified compounds, and which may be potential sources of environmental emissions.



Stage 2

The high priority compounds selected at the conclusion of Stage 1 will be investigated in great detail using the information sources outlined above. Each comprehensive report must give consideration to the following areas:

1. Health Effects:

- (a) Toxicity of specific compounds and dose-response relationships (occupational, environmental).
- (b) Documentation of effects on humans. Source of information (epidemiological surveys, occupational exposure etc.). Special attention should be paid to carcinogenic effects and chronic effects at low dose and extended exposure times.
- (c) Documented instances of community exposure. Population of Ontario potentially affected by specific sources.
- (d) Documentation of effects on animals. Type of test. Dose-response relationships for specific compounds.

2. Process and Control Technology for Reducing Discharges:

- (a) Description and evaluation of available control apparatus. Apparatus appropriate for use by Ontario industries.
- (b) Identification of necessary research and development for improved control and abatement technology.
- (c) Identification of need for data from source discharge monitoring and recommendations for specific programmes.

3. Persistence and Fate of the Pollutant in the Environment

- (a) Decomposition of pollutants in the environment. Other modifications. Characteristics (physical, chemical,



toxicological) after modification.

- (b) Residence time. Dispersal characteristics. Principal removal mechanisms.
- (c) Effect of other substances simultaneously present. Reaction rates.

4. Sampling and Analytical Techniques:

- (a) Description and evaluation of available apparatus and techniques for various parameters (concentrations, particulate size distribution, chemical composition, etc.). Discussion should be compound - specific if necessary.
- (b) Accuracy, sensitivity, and detection limits of available apparatus and techniques. Adequacy of techniques. Identification of research and development needs. Recommendations.
- (c) Apparatus and techniques currently used by Ontario and other major air pollution agencies.

5. Environmental Concentrations:

- (a) Published values of concentrations for specific sources (occupational, ambient environment). Environmental pollution "episodes".
- (b) Environmental concentrations specific to Ontario industries.
- (c) Need for monitoring of concentrations in vicinity of industrial sources and recommendations for specific programmes.

6. Other Effects:

- (a) Description of soiling and corrosion effects. Critical



environmental concentrations and conditions (humidity).

Materials affected. Exposure times.

- (b) Description of odours. Intensity of odour. Recognition threshold for odours (type of test).

7. Standards and Criteria:

- (a) Environmental, point of impingement, and occupational standards and criteria in Ontario and elsewhere. Evaluation.

8. Chemical and Physical Properties of Pollutants:

Discussions must be compound-specific.

9. Recommendations:

Recommendations for further action will include:

- (a) Special surveys in ambient air and water environments - general.
- (b) Special surveys in the vicinity of major sources.
- (c) Emission inventories including source testing programs.
- (d) Epidemiological studies.
- (e) Instrumentation development.

Other relevant topics should not be excluded. Also, the points outlined for each of the above topics are intended only as guides and should not be regarded as restrictive. The Contractor should endeavour to treat each topic as comprehensively as possible. Topics 1,2,3,4,5,9 should be assigned to the highest priority.



6 INTRODUCTION



INTRODUCTION

The "Hazardous Substances Programme" (HASP) was initiated within the Air Resources Branch of the Ontario Ministry of the Environment in 1974. Among the objectives of the program is the creation of a comprehensive information base on selected substances which have been identified as potentially hazardous in Ontario. This would serve as a component for sound rational decision making in future Ministry activities. To date, separate reports have been issued under HASP dealing with asbestos and vinyl chloride monomer. This report deals with a number of light aromatic hydrocarbons: benzene; toluene; ortho-, meta-, and para-xylene; ethylbenzene, cumene, styrene and naphthalene.

The report is divided into a number of key areas in which a thorough review is considered essential in order to derive a reasonable hazard assessment. These include:

- chemical and physical properties
- producers, uses and market forecasts
- process descriptions
- emission and discharge control technology
- sampling and analysis
- environmental persistence and fate
- health effects
- standards



Not included in an overall hazard assessment, but required for the rational development of regulations, are such considerations as alternatives analysis, socioeconomic effects and regulatory options, etc.

This report represents a state-of-the-art review of those key areas listed above with the qualification that only publicly available information was included. No proprietary or confidential information was sought or included.

In order to obtain the information needed, a number of sources were used. These include:

- computer data bases
- scientific and trade journals
- technical manuals and books
- various library holdings
- government publications and reports of government sponsored research
- industrial associations
- leading scientists at universities and other research institutes
- government officials

UNITED TECHNOLOGY and SCIENCE is established as a center for the computer data base searching systems:

- System Development Corporation (ORBIT)
- National Research Council (CAN/OLE)
- National Library of Medicine (MEDLINE)

This allows access to over 50 different data bases. Those bases searched



and found to be of most use include:

- Biosis Previews
- Chemical Abstracts Condensates
- Chemical Industry Notes
- Enviroline
- Federal Register
- National Technical Information Service
- Pollution Abstracts
- Toxline

A number of search strategies were composed and used to scan the various data bases for citations. A total of more than 3,000 citations were drawn. Of these, more than 300 were selected and obtained in full text for a detailed study. In addition to these publications, a number of key scientific journals, trade magazines, technical manuals and books were manually searched for any articles which may have been missed in the computer literature searches. Libraries used include public (Toronto Reference), Universities (University of Toronto, York University, University of Waterloo, and Ryerson College), and government (Ministry of Labor, Ministry of Health, Ministry of the Environment, Atmospheric Environment Service, Environmental Protection Service - Ontario Region and Statistics Canada).

Government publications and publications of work sponsored by government agencies were obtained from the Department of Industry, Trade and Commerce, Statistics Canada, Department of Fisheries and Environment;



Ministry of the Environment, Ministry of Health and Ministry of Labor; and the U.S. EPA. Leading scientists in research institutes and government personnel were visited or telephoned to obtain information on current priorities and as yet unpublished studies.

Trade associations such as the Canadian Chemical Producers Association, Canadian Manufacturers of Chemical Specialties, and The Petroleum Association for the Conservation of the Canadian Environment, were contacted with requests for information in addition to a few specific companies. A form letter requesting information on control equipment for industrial emissions/discharges was sent to over 100 manufacturers and distributors.

All suitable information obtained from the above sources was included in the report.

Each major section of the report was written in such a manner that it is more or less independent of the other sections. Therefore, each is referenced separately. In some sections each compound is considered separately while in others it was considered more suitable to discuss the compounds together.

The Appendix (Section 15) contains a copy of the original "Contractor's Work Programme". During the execution of the study a few, relatively minor, changes in the work program were agreed upon between UNITED TECHNOLOGY and SCIENCE and the Ministry project officer. These changes are reflected in the contents of the report.



7 CHEMICAL AND PHYSICAL PROPERTIES
OF AROMATIC HYDROCARBONS



	SECTION	PAGE NO.
7	CHEMICAL AND PHYSICAL PROPERTIES OF AROMATIC HYDROCARBONS	7-1
7.1	SUMMARY	7-4
7.2	INTRODUCTION	7-5
7.3	BENZENE	7-8
7.3.1	Introduction	7-8
7.3.2	Physical Properties	7-9
7.3.2.1	Structure	7-9
7.3.2.2	Physical Constants	7-10
7.3.3	Chemical Properties	7-13
7.3.3.1	Substitution Reactions	7-13
7.3.3.1.1	Nitration	7-13
7.3.3.1.2	Halogenation	7-15
7.3.3.1.3	Alkylation	7-17
7.3.3.1.4	Acylation	7-19
7.3.3.1.5	Sulfonation	7-21
7.3.3.1.6	Deuteration	7-22
7.3.3.2	Addition Reactions	7-22
7.3.3.3	Oxidation Reactions	7-23
7.3.3.4	Other Reactions	7-24
7.3.3.4.1	Pyrolysis	7-24
7.3.3.4.2	Chloromethylation (Blanc Reaction)	7-24
7.3.3.4.3	Mercuration	7-25
7.3.3.4.4	Metalation	7-25
7.4	TOLUENE	7-26
7.4.1	Introduction	7-26
7.4.2	Physical Properties	7-26
7.4.3	Chemical Properties	7-30
7.4.3.1	Substitution Reactions	7-32
7.4.3.1.1	Nitration	7-32
7.4.3.1.2	Halogenation	7-33
7.4.3.1.3	Alkylation	7-34
7.4.3.1.4	Acylation	7-35
7.4.3.1.5	Sulfonation	7-36
7.4.3.2	Reactions at the Methyl Group	7-38
7.4.3.2.1	Halogenation	7-38
7.4.3.2.2	Oxidation	7-39
7.4.3.2.3	Dealkylation	7-40
7.4.3.3	Other Reactions	7-41
7.4.3.3.1	Disproportionation and Transalkylation	7-41
7.4.3.3.2	Chloromethylation (Blanc Reaction)	7-42
7.4.3.3.3	Hydrogenation	7-42



SECTION	PAGE NO.
7.5	XYLENES AND ETHYLBENZENE
7.5.1	Introduction
7.5.2	Physical Properties
7.5.3	Chemical Properties
7.5.3.1	Reactions Involving the Alkyl Groups
7.5.3.1.1	Isomerization
7.5.3.1.2	Disproportionation
7.5.3.1.3	Dealkylation
7.5.3.1.4	Other Reactions of the Alkyl Groups
7.5.3.2	Reactions of the Aromatic Ring
7.5.3.2.1	Nitration
7.5.3.2.2	Chlorination
7.5.3.2.3	Alkylation
7.5.3.2.4	Sulfonation
7.5.3.2.5	Formaldehyde Reactions
7.5.3.2.6	Reactions with Ammonia
7.3.3	Complex Formation
7.6	CUMENE
7.6.1	Introduction
7.6.2	Physical Properties
7.6.3	Chemical Properties
7.7	STYRENE
7.7.1	Introduction
7.7.2	Physical Properties
7.7.3	Chemical Properties
7.8	NAPHTHALENE
7.8.1	Introduction
7.8.2	Physical Properties
7.8.2.1	Structure
7.8.2.2	Physical Constants
7.8.3	Chemical Properties
7.8.3.1	Substitution Reactions
7.8.3.1.1	Nitration
7.8.3.1.2	Halogenation
7.8.3.1.3	Alkylation
7.8.3.1.4	Acylation
7.8.3.1.5	Sulfonation
7.8.3.1.6	Chloromethylation
7.8.3.2	Addition Reactions
7.8.3.2.1	Hydrogenation
7.8.3.2.2	Chlorine Addition
7.8.3.2.3	Reactions with Polynitro Compounds
7.8.3.3	Ring Rupture
7.9	REFERENCES



7.1 SUMMARY

The physical and chemical properties of the aromatic hydrocarbons, benzene, toluene, xylene isomers, ethylbenzene, cumene, styrene and naphthalene are presented and discussed.

The reactions of these compounds are of four general types: electrophilic substitution reactions, addition reactions, oxidation reactions, and, with the exception of benzene and naphthalene, side-chain reactions. Also, there are some reactions unique to each compound, and these reactions are also described, where applicable.

The reactions of benzene and toluene are described in greatest detail, as the reactions of these compounds serve as examples for the general chemical behaviour of the other compounds considered. An exception is styrene, which because of the reactivity of its olefinic side chain, generally undergoes reactions typical of a substituted ethylene compound.



7.2

INTRODUCTION

Aromatic hydrocarbons derive their name from their pleasant odors. However, these compounds are generally toxic. Aromatic hydrocarbons are highly flammable and burn with a luminous sooty flame, in contrast to alkanes and alkenes, which burn with a clear bluish flame leaving little carbon residue.

Benzene and the other aromatic hydrocarbons have such different properties from typical open-chain conjugated polyenes, such as 1,3,5-hexatriene, that they are considered as a separate class of compounds, generally called arenes.

The unique properties of aromatic hydrocarbons are derived from the stability of the six carbon-atom benzene ring structure, or aromatic nucleus, which is the basic structural unit of these compounds. The physical properties of the aromatic nucleus are discussed under benzene (Section 7.3). The special stability associated with the benzene nucleus is retained in all of the aromatic hydrocarbons discussed here, although small differences due to the substituent alkyl groups exist. Naphthalene is the first member of a series of polynuclear aromatic hydrocarbons having benzene rings condensed in the ortho positions (two rings in the case of naphthalene).

Each of the alkyl substituted aromatic hydrocarbons are systematically named as an alkyl or alkenylbenzene. Thus, toluene is methylbenzene, cumene is 2-propylbenzene, and styrene is ethenylbenzene.

When there are two or more substituents to a benzene ring, position



isomerism arises. Thus, xylene, or dimethylbenzene, has three isomers according to whether the methyl groups are substituted in the 1,2-, 1,3-, or 1,4 positions on the benzene ring. These dimethylbenzene isomers are commonly designated as ortho- (1,2-), meta- (1,3-), or para- (1,4-) xylenes.

Alkyl substituents are referred to as activating and ortho- and para-directing groups. This means that in electrophilic substitution reactions involving alkylbenzenes, the alkyl group activates the ring towards substitution compared to a similar reaction of benzene itself, and causes the substituting group to preferentially react at the ortho- and para- ring positions with respect to the alkyl group ring position. Thus, alkylbenzenes undergo electrophilic substitution under milder conditions than benzene, and the principal products of such reaction are ortho- and para- disubstituted alkylbenzenes.

The naphthalene double-ring nucleus is less stable than the benzene ring, and thus naphthalene undergoes electrophilic substitution under milder conditions than benzene.

Electrophilic substitution reactions are the most important reactions of the aromatic hydrocarbons discussed here. Other reactions undergone are addition reactions, oxidation reactions, and, for the alkyl benzenes, side-chain reactions.

The detailed chemical and physical properties outlined in the following sections for each compound are important in assessing the potential environmental impact of existing or new processes and/or control technologies in use and to properly assess alternative technologies. Those



chemical and physical properties which are important in considering the environmental fate and persistence of the compounds of interest in the ambient environment are discussed in more detail in Chapter 12.



7.3 BENZENE

7.3.1 INTRODUCTION

Benzene (C_6H_6) is a volatile, colorless, and flammable liquid aromatic hydrocarbon which has a very characteristic odor.

Benzene is used principally as a chemical raw material in the synthesis of compounds such as styrene, phenol, dodecylbenzene, nitrobenzene, cyclohexane, nonylphenol, chlorobenzene, benzene hexachloride, and maleic anhydride. Benzene is also used as a solvent.

Benzene, or "bicarburet of hydrogen", was first isolated by Faraday in 1825, who obtained it from a liquid condensed by compressing oil gas. In 1833 Mitscherlich obtained "bicarburet of hydrogen" by distilling benzoic acid with lime and suggested the name "benzin" for the compound. Leibig disagreed with this name and suggested "benzole". Benzene was found by A.W. Hoffman in light oil derived from coal tar in 1845. The commercial recovery of benzene from this source was developed and described by Mansfield in 1849. The synthesis of benzene by the polymerization of acetylene was first carried out by Berthelot in 1866.

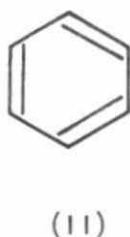
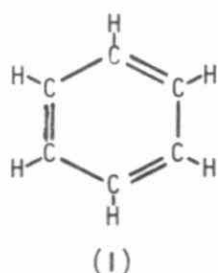
The pure compound is now called benzene, the name approved by the International Union of Pure and Applied Chemistry (IUPAC). The term 'benzol' has long been used for commercial products predominantly containing benzene, but this term is now declining in use.



7.3.2 PHYSICAL PROPERTIES

7.3.2.1 STRUCTURE

The structure of benzene is usually represented by the Kekulé ring formula (I), often abbreviated to (II). Formula (III) gives a more realistic picture of the molecular structure and is now the most commonly used representation.



The benzene molecule is planar, with all of the carbon atoms in a single plane. The six carbon atoms form a regular hexagon in which each carbon atom is 0.139 nm distant from each of the two adjacent carbon atoms. Each hydrogen atom is 0.108 nm distant from the carbon atom to which it is bonded.

The heat of formation for benzene can be calculated using approximate methods based on the molecular structures represented above as (I) or (II). Experimental evidence, however, indicates the molecule is more stable than calculated by about 151 kJ/mol. This extra stability is the result of the different resonant structures which may be used to represent bonding within the molecule and is referred to as resonance energy. As indicated above, all carbon-carbon bonds are of equal length and these are intermediate between the usual carbon-carbon single and

double bonds found in non-aromatic organic compounds.

Quantum-mechanical calculations predict this resonance energy and the observed bond lengths with good accuracy, and indicate that the bonding π -electrons are distributed in doughnut shaped orbitals above and below the plane of the molecule.

7.3.2.2 PHYSICAL CONSTANTS

Table 7-1 lists the physical properties of benzene (1). Benzene forms a two phase, minimum-boiling-point, azeotropic mixture with water. At a pressure of 101.3 kPa, the boiling point of the mixture is 69.25 °C and the vapor contains 8.83 wt. % of water.

The water solubility and vapor pressure are significant parameters in the environmental chemistry of benzene. These parameters are temperature dependent and may be affected by various environmental conditions.

McAuliffe (2) has reviewed a number of reported values (1730-1790 ppm) for the solubility of benzene in water. The variation is probably attributable to temperature differences or differences in precision of the techniques used. Both salting-in and salting-out (increase and decrease in solubility) effects have been noted for benzene in aqueous solutions (3). Sutton and Calder (4) have noted a decrease in the solubility of higher molecular weight n-paraffins in salt water compared to distilled water. A similar decrease occurs with the water soluble fraction (including benzene) of crude oils (5). Thus, the solubility of benzene in water containing dissolved salts (eg river water, plant



TABLE 7-1

PHYSICAL PROPERTIES OF BENZENE

Molecular Formula	C_6H_6
Physical State	Liquid
Molecular Weight, g	78.11
Melting Point, °C	5.533
Boiling Point, °C	80.103
Density, at 25 °C, g/cm^3	0.8787
Refractive Index, n_D^{25}	1.49792
Viscosity (absolute at 20 °C), mPa.s	0.6468
Surface Tension at 25 °C, mN/m	28.18
Vapor Pressure at 26.075 °C, kPa	13.33
Flash Point (closed cup), °C	-11.1
Ignition Temperature in Air, °C	538
Critical Temperature, °C	289.45
Critical Pressure, MPa	4.9244
Critical Density, g/cm^3	0.300
Flammability Limits in Air, vol %	1.5 - 8.0
Heat of Fusion, kJ/mol	9.837
Heat of Vaporization at 80.103 °C, kJ/mol	33.85
Heat of Combustion at Constant Pressure and 25 °C (liq. C_6H_6 to liq. H_2O and gaseous CO_2), kJ/g	41.836
Solubility in Water, 25 °C	0.180 g/100 g
Solubility of Water in Benzene, 25 °C	0.05 g/100 g
Vapor Density (air = 1)	2.7
Percent in Saturated air (101.325 kPa), 26 °C	13.15
Density of Saturated Vapor-Air Mixture at 101.325 kPa (air = 1), 26 °C	1.22



TABLE 7-1 (cont.)

C.A.S. Registry Number	71-43-2
Synonyms	Benzol Coal Naphtha Cyclohexatriene Phene Phenyl Hydride Pyrobenzole Benzole (6) Annulene



effluents, sea water) is probably less than the reported distilled water value.

The variation of benzene vapor pressure with temperature is presented in Table 7-2 (6). The vapor pressure of benzene is appreciable at ambient temperature (26 °C), 13.33 kPa. Calculations performed by MacKay and Wolkoff (7) indicate that the rate of evaporation of benzene from water bodies could be appreciably higher than indicated from simple vapor pressure calculations. They calculated a half-life for the decrease in concentration of benzene in water of 1 m depth by evaporation to be 37 minutes. This is of great significance during sampling and analysis of polluted waters, since significant amounts of benzene may evaporate or have already evaporated from the water source.

Benzene is miscible with several common solvents such as methanol, chloroform, acetone, carbon tetrachloride, and many hydrocarbons.

7.3.3 CHEMICAL PROPERTIES

The reactions of benzene may be divided into: substitution, addition, and cleavage or rupture of the ring. Examples of all three types of reactions are used industrially, although most reactions of industrial importance are of the substitution type.

7.3.3.1 SUBSTITUTION REACTIONS

7.3.3.1.1 NITRATION

Nitration of benzene in mixtures of nitric and sulfuric acids is not usually brought about by attack of a nitric acid molecule on the benzene ring, but by attack of the more electrophilic species, the nitronium ion, NO_2^+ . There is evidence to show that this ion is formed from nitric acid and sulfuric acid according to the following equation:



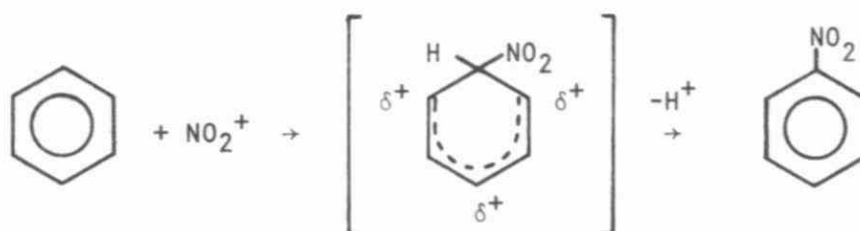
TABLE 7-2
VAPOR PRESSURE-TEMPERATURE RELATIONSHIP
FOR BENZENE

<u>TEMPERATURE, °C</u>	<u>VAPOR PRESSURE, kPa</u>
-36.7	0.133
-19.6	0.667
-11.5	1.333
- 2.6	2.666
7.6	5.333
15.4	7.999
26.1	13.332
42.2	26.665
60.6	53.330
80.1	101.325





The nitronium ion then attacks the aromatic ring to give nitrobenzene.



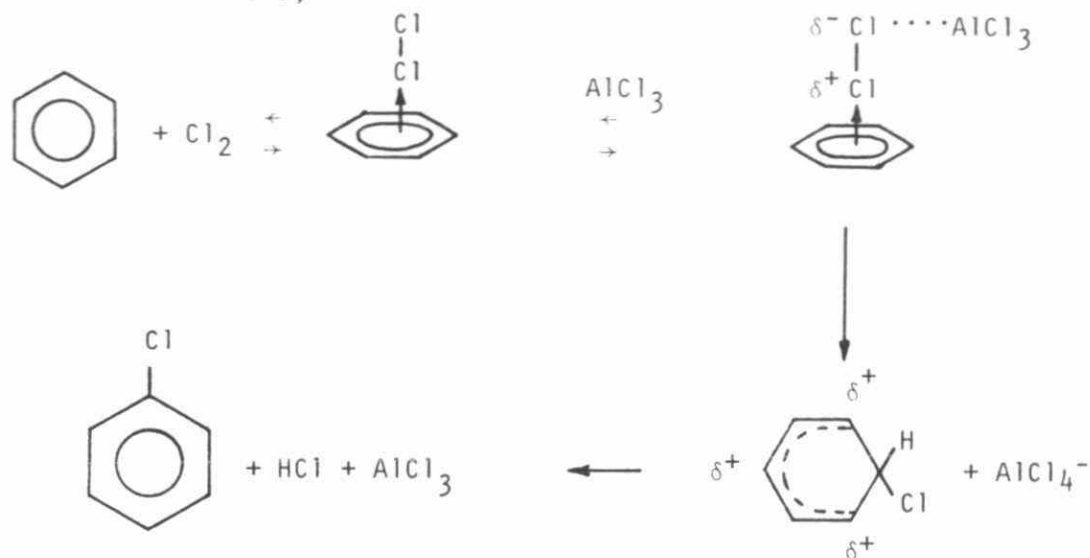
The yield from this reaction can be as high as 98 % using a nitric acid/sulfuric acid mixture at 50-55 °C. Because nitration is hindered by the meta-directing nitro group, dinitrobenzene is not normally obtained in significant quantity, but can be produced (chiefly the meta-isomer) by using more vigorous conditions. With a mixture of fuming nitric and fuming sulfuric acids, 1,3,5-trinitrobenzene can be obtained.

7.3.3.1.2 HALOGENATION

The mechanism of halogenation is complicated by the fact that molecular halogens, Cl_2 , Br_2 , and I_2 , form 1:1 charge-transfer complexes with benzene. Although this complex formation assists substitution by bringing the reactants in close proximity, it does not always follow that a substitution reaction will occur. A catalyst is usually necessary, and the catalysts most frequently used are metal halides that are capable of accepting electrons (eg FeBr_3 , AlCl_3 , and ZnCl_2). Their catalytic activity may be attributed to their ability to polarize the halogen-halogen bond.



The positive end of the halogen dipole attacks the benzene ring while the negative end is complexed with the catalyst. The reaction can be represented as follows,



the slow step in this reaction being formation of a σ bond between Cl^+ and the aromatic ring.

The order of reactivity of the halogens is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

Fluorine is too reactive for direct preparation of fluorobenzenes, and indirect methods are necessary. Iodine is unreactive unless it is converted to a more active species with an oxidizing agent such as nitric acid.

Halogenation can also be carried out using hypochlorous and hypobromous acids, which are most reactive when a strong acid is present and care is taken to exclude formation of halide ions. The positive ions H_2OCl^+ and



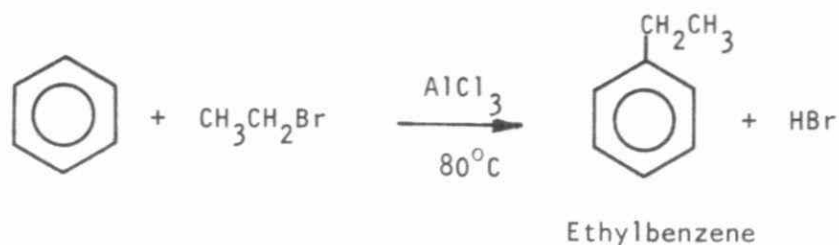
H_2OBr^+ are powerfully electrophilic and are considered to be the reactive agents.

Chlorobenzene is produced commercially by passing dry chlorine into benzene in the presence of a catalyst (eg molybdenum chloride) at atmospheric pressure and moderate temperature. A continuous process in which an excess of benzene is used slightly below its boiling point results in chlorination in a ratio of 14 parts of monochloro- to 1 part of dichlorobenzene.

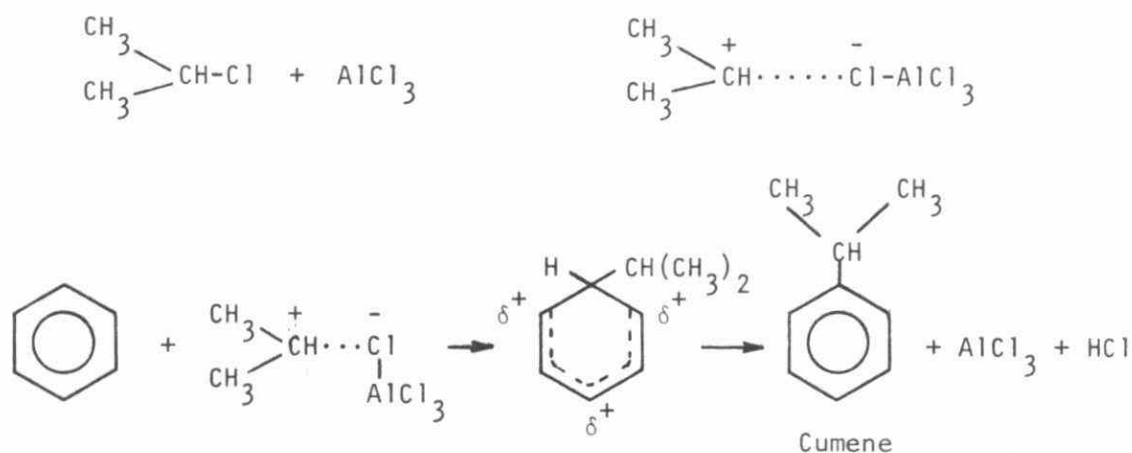
In sunlight and in the absence of oxygen and substitution catalysts, chlorine and bromine add to benzene, forming benzene hexachloride (hexachlorocyclohexane, $\text{C}_6\text{H}_6\text{Cl}_6$) and benzene hexabromide (hexabromocyclohexane, $\text{C}_6\text{H}_6\text{Br}_6$) respectively. Five stereoisomers of benzene hexachloride are obtained when chlorine is added to benzene in the presence of actinic light. The gamma isomer, formed in 10-12 % yield, is used as an insecticide.

7.3.3.1.3 ALKYLATION

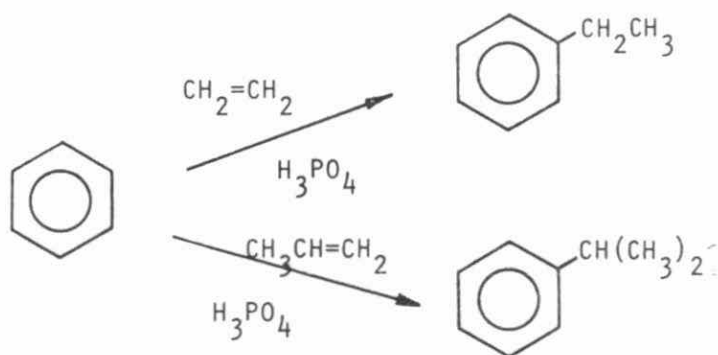
An important method of synthesis of alkylbenzenes utilizes an alkyl halide as the alkylating agent together with a metal halide catalyst, usually aluminium chloride.



This class of reaction is familiarly known as Friedel-Crafts alkylation. The metal halide catalyst functions in a similar way to halogenation reactions; it provides a source of a positive substituting agent, which in this case is a carbonium ion.



Alkylation can also be carried out using alcohols and alkenes in the presence of acidic catalysts such as phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), hydrofluoric acid (HF), boron trifluoride (BF_3), or HF-BF_3 . Ethylbenzene is made commercially from benzene and ethylene using H_3PO_4 as catalyst. Cumene is prepared similarly from benzene and propylene.



Under these conditions, the carbonium ion is generated by protonation of the alkene.

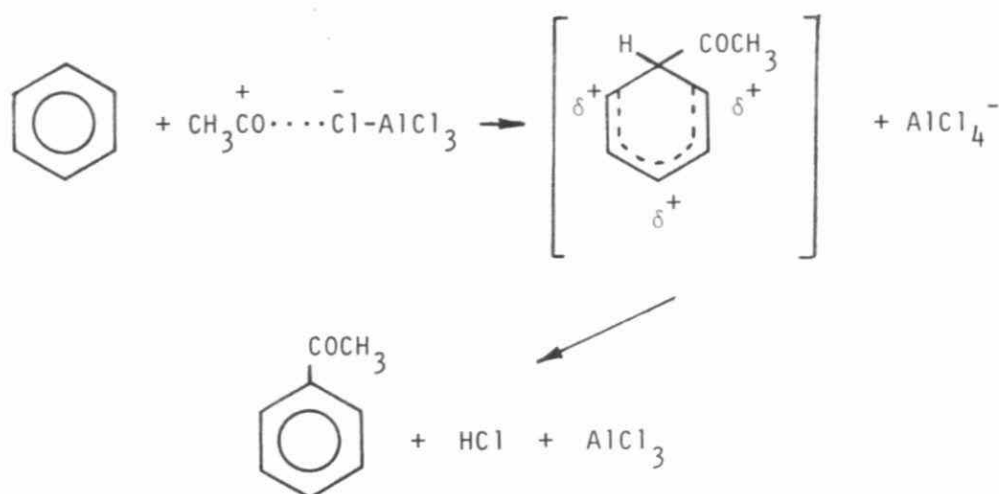


There are several factors that limit the usefulness of alkylation reactions. First, it may be difficult to limit reaction to mono-substitution because introduction of one alkyl substituent activates the ring towards substitution of a second alkyl group. Thus in order to obtain good yields of monoalkylbenzenes, a large excess of benzene must be used. A second limitation is the tendency for the alkylating reagent to give rearrangement products. For example, the alkylation of benzene with n-propyl chloride gives a mixture of n-propyl and isopropyl benzene. This is because the first formed n-propyl carbonium ion can either react with benzene or rearrange to the more stable isopropyl carbonium ion, which then reacts with benzene.

7.3.3.1.4 ACYLATION

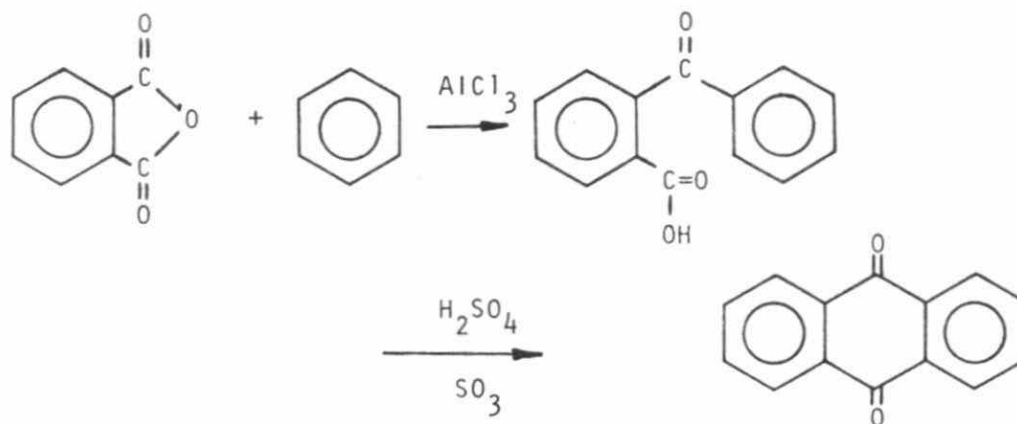
Acylation and alkylation reactions of benzene are closely related. The reaction introduces an acyl group, $\text{RCO}-$, into the aromatic ring, and the product is a phenyl ketone. The acylating reagents commonly used are acid halides, RCOCl , or anhydrides, $(\text{RCO})_2\text{O}$. The catalyst is usually aluminium chloride, and its function is to generate the active substituting agent, which probably is an acyl cation.



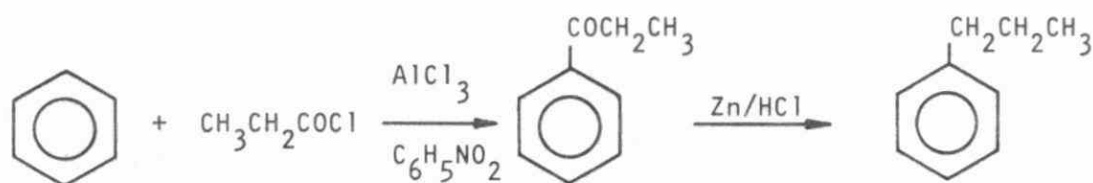


Acylation differs from alkylation in that the reaction is carried out in a solvent, commonly carbon disulfide or nitrobenzene. Also, acylation requires more catalyst than alkylation since much of the catalyst is removed by complex formation with the product ketone.

Friedel-Crafts acylation is limited to mono-substitution. An illustration of this is the synthesis of anthraquinone from benzene and phthalic anhydride by way of o-benzoylbenzoic acid. Aluminium chloride is not a sufficiently powerful reagent to catalyse the second step and the use of fuming sulfuric acid is necessary.

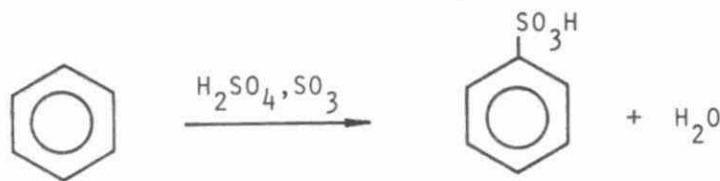


Because acylation is limited to monosubstitution, it is sometimes best to prepare alkylbenzenes by acylation followed by reduction of the carbonyl group. An example of this is the preparation of n-propyl benzene, since the direct alkylation of benzene with n-propyl chloride yields a large amount of by-product cumene.



7.3.3.1.5 SULFONATION

Substitution of benzene by the sulfonic acid group ($-\text{SO}_3\text{H}$) is usually carried out by heating the hydrocarbon with a slight excess of concentrated or fuming sulfuric acid.

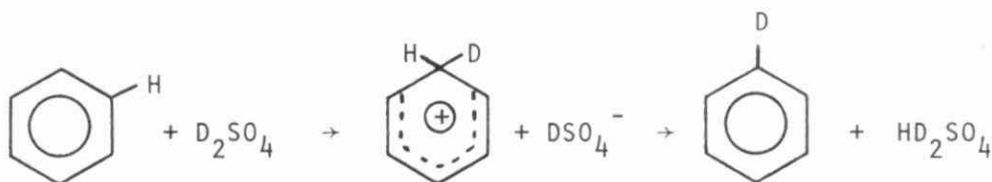


The reaction is usually carried out at temperatures sufficiently high (170-180 °C) to evaporate water produced in the reaction. A second group can be introduced by reaction with fuming sulfuric acid at higher temperatures, although the reaction is hindered by the presence of the

first group. The principal product is m-benzene disulfonic acid, with a small amount of p-benzene disulfonic acid being formed.

7.3.3.1.6 DEUTERATION

It is possible to replace the ring hydrogens of benzene with deuterium by exchange with deuteriosulfuric acid. The mechanism is analogous to other electrophilic substitutions.



Perdeuterobenzene (C_6D_6) can be made from benzene in good yield if a large excess of deuteriosulfuric acid is used. Deuteration occurs under very mild conditions, and thus no sulfonation of the benzene occurs.

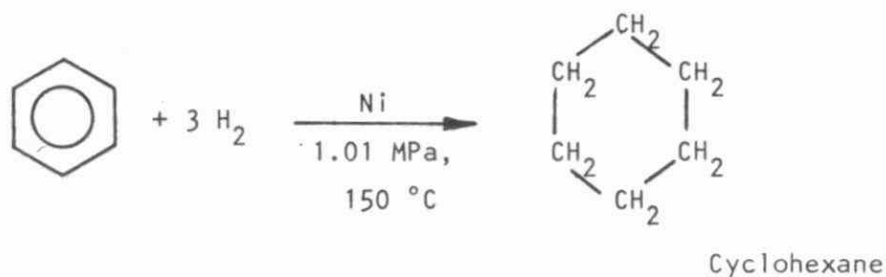
7.3.3.2 ADDITION REACTIONS

The benzene ring is not readily converted to a saturated six-membered ring, but some of the few addition reactions that are possible are carried out on a large scale industrially.

The photochemical chlorination of benzene to give benzene hexachloride ($\text{C}_6\text{H}_6\text{Cl}_6$) has already been discussed. Benzene may be hydrogenated to cyclohexane in the presence of a nickel catalyst. The reaction is of

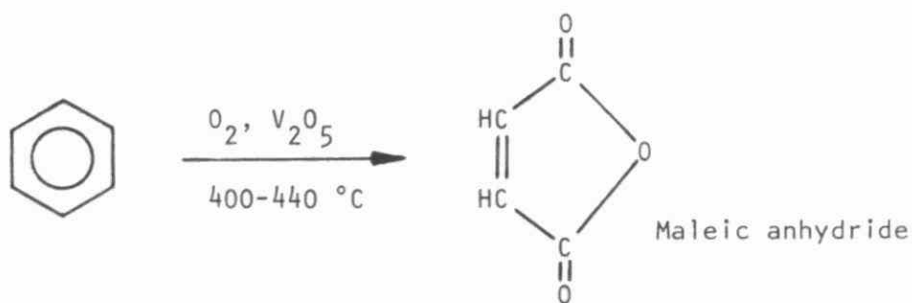


commercial importance, as cyclohexane is widely used as a solvent and in the synthesis of adipic acid and caprolactam, which are intermediates in the synthesis of nylon.



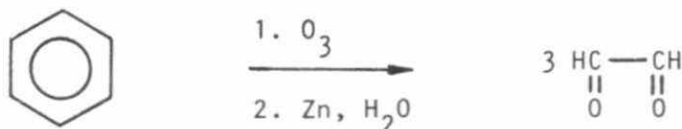
7.3.3.3 OXIDATION REACTIONS

At high temperatures, benzene can be oxidized to maleic anhydride by air, with a vanadium pentoxide catalyst. This anhydride is prepared on a large scale for use in the production of polyesters.



Benzoquinone has been reported as a by-product of benzene oxidation at 410-430 °C. Benzene is oxidized in the vapor phase to phenol in low yield at 450-800 °C with air and without catalyst.

Ozonization of benzene is possible, with the product being glyoxal.



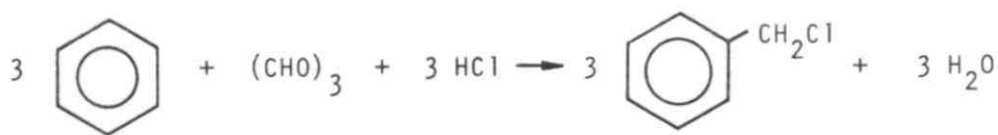
7.3.3.4 OTHER REACTIONS

7.3.3.4.1 PYROLYSIS

When benzene (in the absence of O_2) is passed through a red-hot tube, bubbled through molten lead or pumice, or passed at elevated temperatures over vanadium compounds, condensation takes place with the formation of biphenyl. Smaller amounts of p-diphenylbenzene, 1,3,5-triphenylbenzene, and 4,4-diphenylbiphenyl are also formed. At temperatures above 750°C , benzene decomposes, largely into carbon and hydrogen.

7.3.3.4.2 CHLOROMETHYLATION (BLANC REACTION)

Benzene reacts with formaldehyde and hydrochloric acid in the presence of zinc chloride to yield benzyl chloride.



7.3.3.4.3 MERCURATION

Mercuric acetate and benzene react under reflux to form phenyl mercuric acetate.

7.3.3.4.4 METALATION

Benzene reacts with alkali metal derivatives such as ethylsodium to yield alkali metal derivatives of benzene (eg phenylsodium). The reaction occurs poorly for benzene itself, but is very useful for aromatic ethers. The usual metalating agent for these compounds is n-butyl lithium.



7.4 TOLUENE

7.4.1 INTRODUCTION

Toluene ($C_6H_5CH_3$) is a clear, colorless, refractive, non-corrosive liquid, with a distinctive aromatic odor similar to but milder than benzene. It is highly flammable and burns with a luminous, sooty flame leaving a carbon residue. Toluene is a homologue of benzene in which one hydrogen atom has been replaced by a methyl group.

Toluene is used in both the chemical and pharmaceutical industries, either as a starting material or as an intermediate in chemical synthesis. It is used as an intermediate in the manufacture of trinitrotoluene, benzaldehyde, benzene, benzoic acid, and phenol. Toluene is also used as a thinner for paints, varnishes and laquers, and as a constituent of motor and aviation fuel.

Toluene was originally discovered in studies evaluating the degradation products obtained by heating a natural resin, the balsam of Tolu, named for a small town in Columbia, South America. This balsam was used as a medicinal and in perfumery. The discovery of toluene is credited to Pelletier and Walter in 1835.

7.4.2 PHYSICAL PROPERTIES

The physical and thermodynamic properties of toluene are presented in Table 7-3 (8).

Azeotropes are important in the purification of toluene, in solvent technology, and in the recovery of toluene from reaction mixtures. The most important azeotropes of toluene are listed in Table 7-4 (8). All



TABLE 7-3
PHYSICAL PROPERTIES
OF TOLUENE

Molecular Formula	$C_6H_5CH_3$
Physical State	Liquid
Molecular Weight, g	92.13
Boiling Point, °C	110.623
Freezing Point, °C	-94.991
Vapor Pressure at 26.04 °C, kPa	4.00
at 25 °C	3.73
Specific Gravity, g/cm ³	0.86220
Vapor Density (air = 1)	3.14
Percent in Saturated Air (101.3 kPa)	3.94 (26 °C)
Density of Saturated Vapor-Air Mixture at 101.3 kPa (air = 1)	1.09 (26 °C)
Solubility in Water, g/100 cm ³ at 16 °C	0.047
Solubility of Water in Toluene, mol % at 10 °C	0.006
Flammability Limits (% by vol. in air)	1.17 - 7.10
Flash Point (closed cup), °C	4.44
Autoignition Temperature, °C	552
Refractive Index, n_D^{20}	1.497
Partition Coefficient (octanol/water)	2.5825 average
Odor Threshold in Air, ppm	4.68 (coke derived) 2.14 (petroleum derived)
Dipole Moment, e.s.u.	0.36×10^{18}
Surface Tension, mN/m (20 °C)	28.53
Heat of Vaporization, kJ/mol	38.0
Heat of Formation, kJ/mol	50.0 (gas) 12.0 (liquid)
Critical Temperature, °C	320.8



TABLE 7-3 (cont.)

Critical Pressure, MPa	4.052
Critical Density, g/cm ³	0.29
C.A.S. Registry Number	108-88-3
Synonyms	Methylbenzene Phenylmethane Toluol Methylbenzol Methacide



TABLE 7-4

AZEOTROPES OF TOLUENE

<u>COMPONENT</u>	<u>bp, °C</u>	<u>AZEOTROPE COMPONENT Wt %</u>	<u>TOLUENE Wt %</u>
Paraffins			
- 2,5-dimethylhexane	107.0	65	35
- 2,3,4-trimethylpentane	109.5	40	60
- 2-methylheptane	110.3	18	82
- n-octane		nonazeotrope	
Naphthenes			
- methylcyclohexane		nonazeotrope	
- ethylcyclopentane	103.0	93	7
- 1,1,3-trimethylcyclopentane	103.8	84	16
- cis, trans, cis-1,2,4-trimethylcyclopentane	107.0	61	39
- cis, trans, cis-1,2,3-trimethylcyclopentane	108.0	61	39
- cis, 1,3-dimethylcyclohexane	110.6	4	96
Hydroxyl Compounds			
- methyl alcohol	63.8	69	31
- ethyl alcohol	76.7	68	32
- isopropyl alcohol	80.6	58	42
- n-propyl alcohol	92.6	43	57
- water	84.1	13.5	86.5
- sec-butyl alcohol	95.3	55	45
- n-butyl alcohol	105.5	32	68
- 2-pentanol	107	28	72
- 3-pentanol	106 ^a	35 ^a	65

^a Approximate Value

of these azeotropes are minimum boiling, ie the boiling point of the azeotrope is below that of either of the two pure components. Ternary azeotropes are also known, largely azeotropes with aqueous alcohols.

The variation of toluene vapor pressure with temperature is presented in Table 7-5 (8). The vapor pressure of toluene at ambient temperature (25 °C) is 3.73 kPa (28 mm Hg). This is lower than the corresponding pressure for benzene (13.3 kPa), so toluene is not expected to evaporate as quickly as benzene. However, the rate of evaporation of toluene from water bodies has been calculated (7), and is much higher than expected from vapor pressure calculations alone. This is due to the high activity coefficient of toluene in water which causes a high equilibrium vapor partial pressure and a higher rate of evaporation. The half-life for the decrease in concentration of toluene in water of 1 m depth, assuming a water evaporation rate of $2740 \text{ g/m}^2 \text{ day}$, was calculated to be 30.6 minutes (7). Comparison of this figure with benzene shows that toluene evaporates faster than benzene from water.

7.4.3 CHEMICAL PROPERTIES

The reactions of toluene are similar to those of benzene. However, substitution reactions occur faster with toluene than with benzene because of an activating effect of the methyl group. Also there are additional possibilities for reactions at the methyl group, and such reactions do occur.

The methyl group in toluene activates the aromatic ring towards electrophilic substitution, and directs the substitution predominantly



TABLE 7-5
VAPOR PRESSURE-TEMPERATURE RELATIONSHIP
FOR TOLUENE

<u>TEMPERATURE, °C</u>	<u>VAPOR PRESSURE, kPa</u>
6.36	1.33
18.38	2.67
26.03	4.000
31.76	5.33
36.39	6.67
40.31	8.00
46.73	10.67
51.94	13.33
61.94	20.00
69.50	26.66
80.84	40.00
89.48	53.30
96.51	66.66
102.51	79.99
107.76	93.33
110.62	101.33

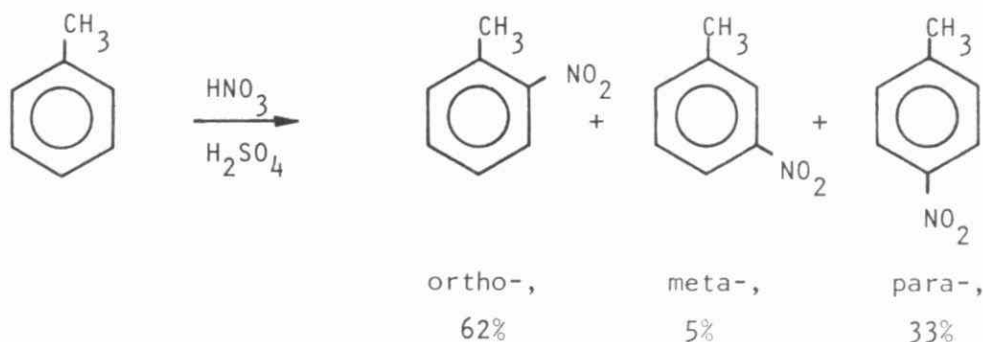


to the ortho- and para- positions on the ring. Thus toluene undergoes electrophilic aromatic substitution reactions faster than benzene and under milder conditions.

7.4.3.1 SUBSTITUTION REACTIONS

7.4.3.1.1 NITRATION

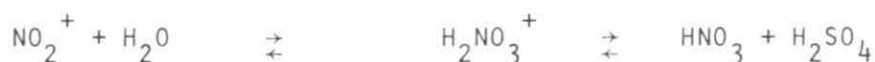
Nitration of toluene is normally carried out with strong nitric acid in the presence of concentrated sulfuric acid in a 1:2 ratio. The products are a mixture of ortho, meta, and para- nitrotoluenes, predominantly the ortho and para-substituents.



The attacking electrophilic reagent is the nitronium ion, NO_2^+ , formed according to the equation:



The presence of any appreciable concentration of water in the reaction mixture is deleterious, since water tends to reverse the reaction by which the nitronium ion is formed.

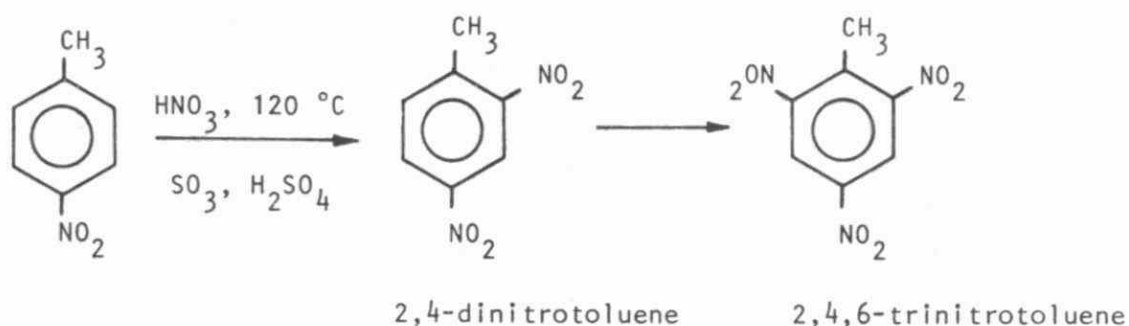


The fact that more dilute nitric acid can be used in the nitration of toluene than for benzene, illustrates the activating effect of the



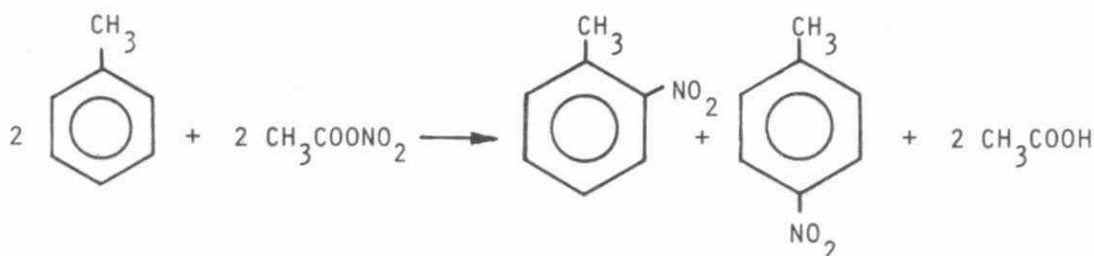
methyl group on the aromatic ring compared to benzene.

Using fuming nitric acid and fuming sulfuric acid, the nitrotoluenes, which are far less reactive than toluene, can be nitrated further to dinitrotoluenes and trinitrotoluene.



The above reaction is of importance in the manufacture of explosives.

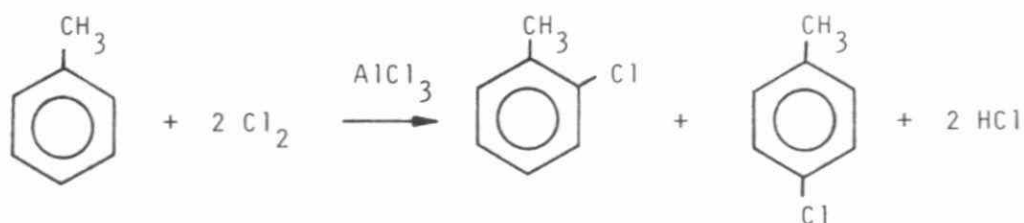
Nitration of toluene can also be carried out using acetyl nitrate in acetic anhydride solution at 0 °C.



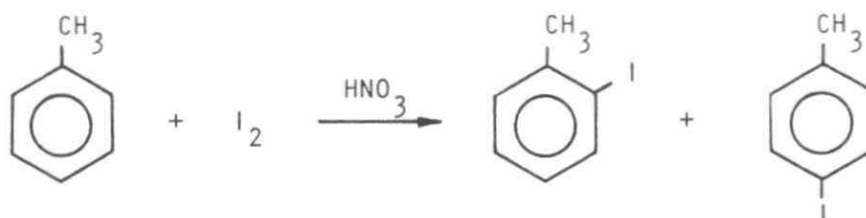
7.4.3.1.2 HALOGENATION

In the presence of a catalyst, and in the absence of light, toluene is halogenated to give a mixture of ortho- and para- halo-toluenes.





Iodination of toluene is usually carried out in the presence of an oxidizing agent, eg nitric acid.



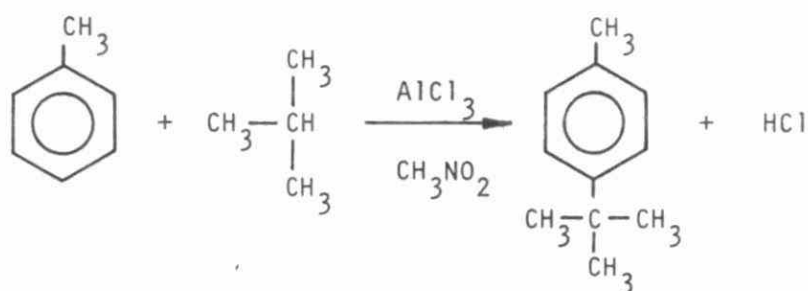
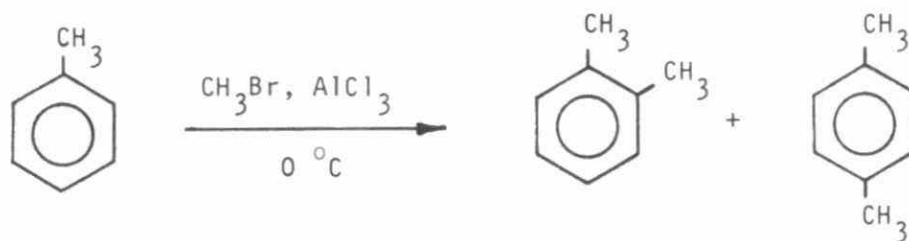
Fluorine is too reactive to be of practical use for the preparation of fluorotoluene compounds and indirect methods are necessary.

Halogenation must be carried out in the absence of light, as toluene will react rapidly with the halogen by a photochemical process to substitute hydrogens of the methyl group rather than the aromatic ring.

7.4.3.1.3 ALKYLATION

Toluene can be readily alkylated in the presence of an appropriate acidic catalyst, eg AlCl_3 , H_3PO_4 , H_2SO_4 , HF , BF_3 .



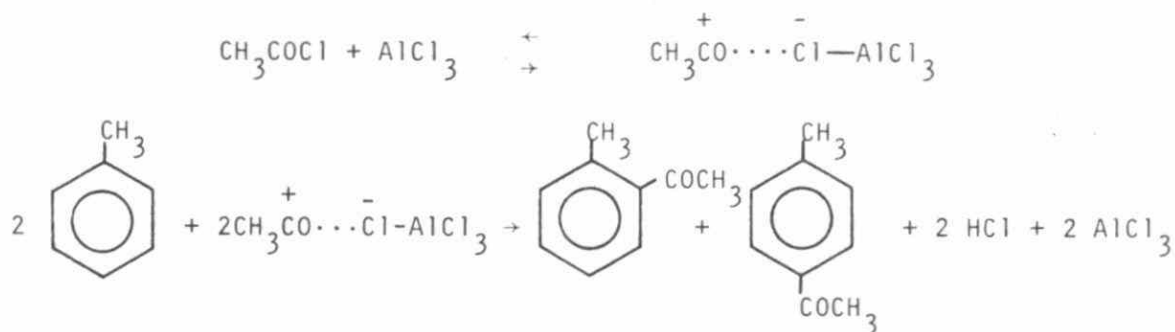


An excess of toluene must be used in these reactions to minimize further substitution caused by activation of the ring. Also, toluene and its alkylation products tend to disproportionate and isomerize in the presence of large amounts of catalyst. This reaction is discussed further below.

7.4.3.1.4 ACYLATION

This reaction introduces an acyl group, RCO- , into the ring and the product is an aromatic ketone. The acylating reagents commonly used are acid halides RCOCl , or anhydrides, $(\text{RCO})_2\text{O}$. The catalyst is usually a substituting agent. This reaction may be carried out at 0°C .

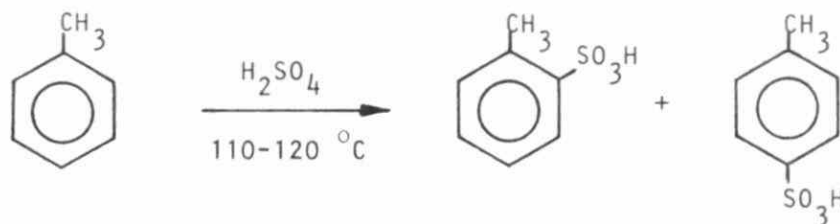




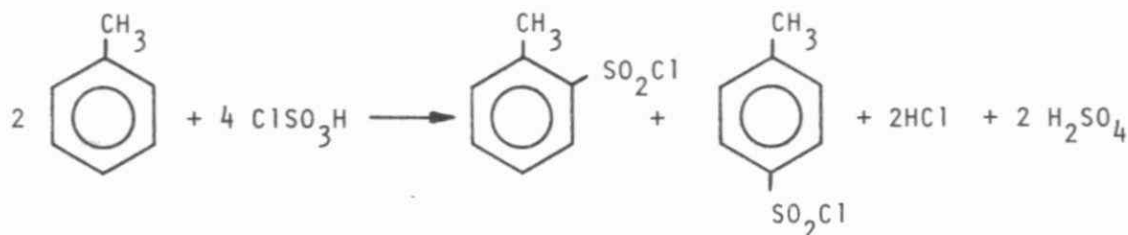
Acylation differs from alkylation in that the reaction is usually carried out in a solvent, eg carbon disulfide or nitrobenzene. Disubstitution is not a problem because of the large deactivating effect of an acyl group on the aromatic ring.

7.4.3.1.5 SULFONATION

Substitution of toluene by a sulfonic acid group ($-\text{SO}_3\text{H}$) is normally carried out by heating toluene with a slight excess of concentrated sulfuric acid in a nitrobenzene solvent. The products are a mixture of ortho- and para- toluene sulfonic acids.



A useful alternative preparation of sulfonyl derivatives of toluene is by the use of chlorosulfonic acid.

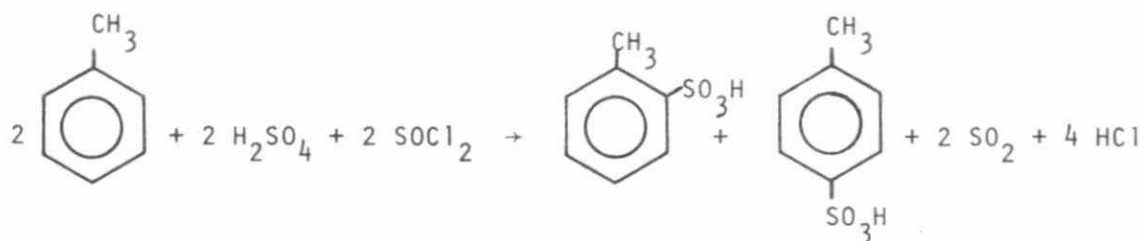


This procedure has the advantage over direct sulfonation in that the sulfonyl chlorides are soluble in organic solvents and may be easier to separate from the reaction mixture than the corresponding sulfonic acids. The sulfonyl chloride derivatives can be easily converted to sulfonic acids by hydrolysis.



A method for achieving sulfonation without the use of an excess of sulfuric acid is to use thionyl chloride to destroy the water formed in the reaction.

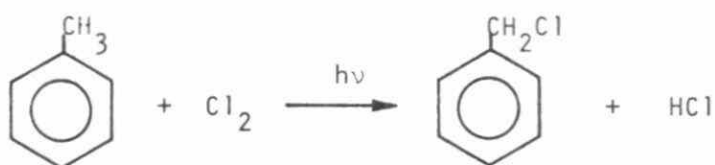




7.4.3.2 REACTIONS AT THE METHYL GROUP

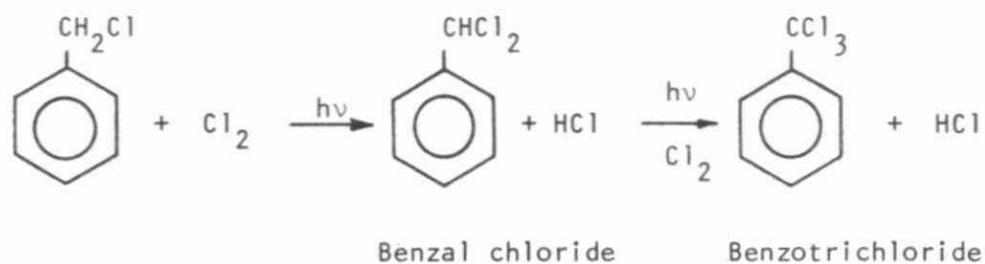
7.4.3.2.1 HALOGENATION

In the presence of actinic light, halogens will react with the methyl group of toluene by a photochemical process to substitute methyl hydrogen atoms rather than the aromatic ring. Chlorination by this process is of industrial importance in the production of benzyl chloride.



Benzyl chloride can be further chlorinated by the same process to yield benzal chloride and benzotrichloride.





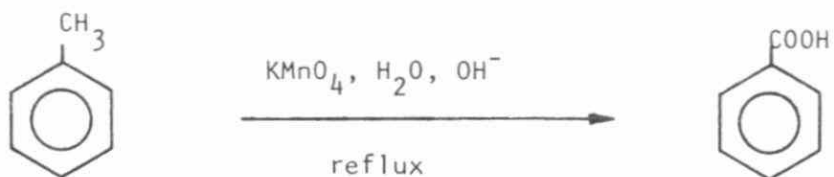
By the appropriate choice of reaction conditions, any one of these three chlorination compounds can be obtained in good yield.

7.4.3.2.2 OXIDATION

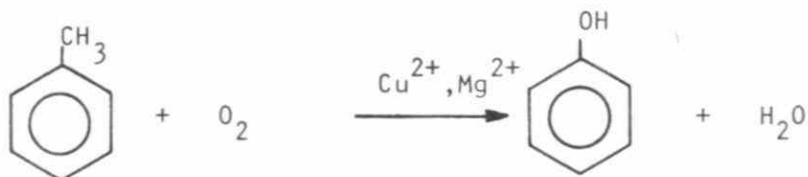
Toluene is oxidized in the liquid phase with air to give benzoic acid as the principal product. Catalysts are generally used in this reaction industrially.



The oxidation of toluene can also be carried out using potassium permanganate or potassium dichromate.



Toluene can also be oxidized to phenol. This reaction is carried out commercially.



7.4.3.2.3 DEALKYLATION

The most important reaction of toluene commercially is hydrodealkylation to benzene. This reaction can be carried out thermally or catalytically.



A number of commercial processes are used to carry out this reaction. They are all vapor-phase processes carried out at high temperatures under pressures of greater than 2 MPa.

Under appropriate thermal conditions, toluene forms dibenzyl.



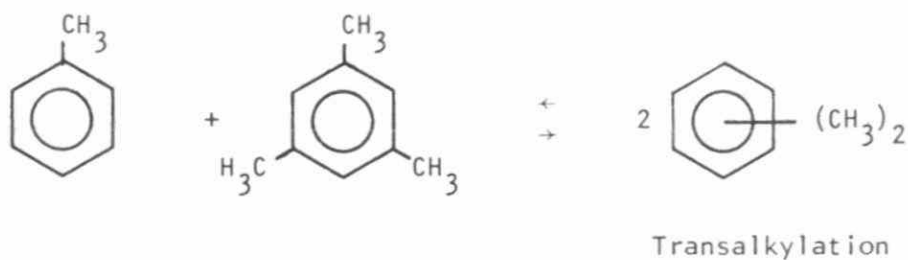
7.4.3.3 OTHER REACTIONS

7.4.3.3.1 DISPROPORTIONATION AND TRANSALKYLATION

These reactions are carried out in the presence of a catalyst. The reactions are reversible and can be carried out either in the liquid or vapor phase.



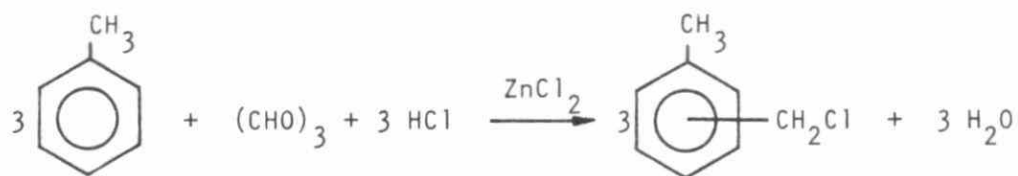
Disproportionation



These reactions often occur as side reactions in the alkylation of toluene.

7.4.3.3.2 CHLOROMETHYLATION (BLANC REACTION)

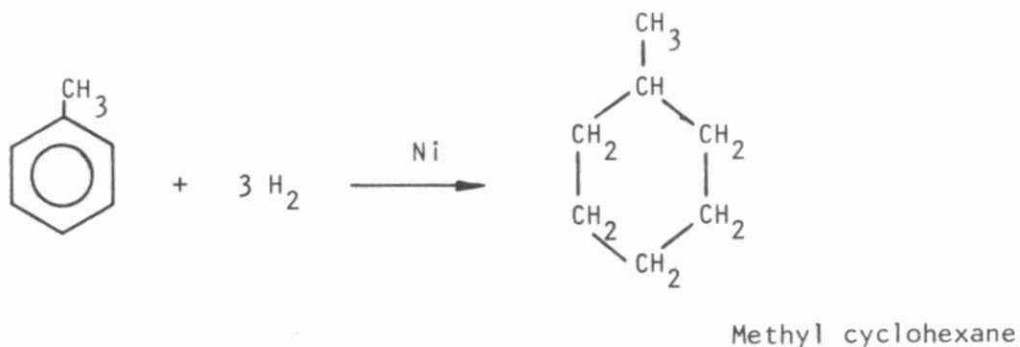
Toluene readily undergoes this reaction with formaldehyde and hydrochloric acid in the presence of aluminium chloride or zinc chloride.



7.4.3.3.3 HYDROGENATION

Toluene can be readily hydrogenated to methylcyclohexane in the presence of a nickel catalyst.





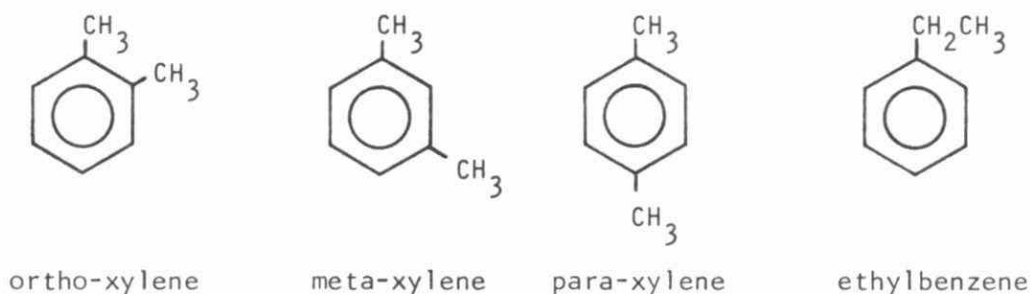
The reverse reaction, ie the dehydrogenation of methylcyclohexane to toluene, is the principal method by which toluene is manufactured. This is the basis of the catalytic reforming process whereby selected naphthenes (cyclic aliphatic hydrocarbons) are dehydrogenated to toluene and other aromatics.



7.5 XYLENES AND ETHYL BENZENE

7.5.1 INTRODUCTION

Xylenes ($C_6H_4(CH_3)_2$) and ethylbenzene ($C_6H_5CH_2CH_3$) are eight carbon atom compounds of the benzene family. The term "xylenes" applies to a mixture of any two or three of the dimethylbenzene isomers, i.e. ortho-, meta- and para-xylenes. All of the xylene isomers and ethylbenzene are clear, colorless, refractive and flammable liquids having characteristic aromatic odors similar to those of benzene and toluene. The structures of these compounds are illustrated below:



The discovery of xylenes is credited to A. Cahours who isolated them in the middle of the 19th century. At about this time, by-product chemicals from coal carbonization were being recovered and this became the principal source of xylenes. Today, xylenes are principally recovered from the reformat fraction of oil refineries, as co-products with benzene and toluene.

Each of the xylene isomers finds its principal use in the manufacture of one particular product. Ethylbenzene is primarily employed as a



raw material to manufacture styrene. Ortho-xylene is used principally to manufacture phthalic anhydride, meta-xylene to manufacture isophthalic acid, and para-xylene to manufacture terephthalic acid. These phthalic acids and derivatives are used to produce plasticizers for the plastics and synthetic resins industry, particularly for polyester fibre manufacture.

Although ethylbenzene is a significant component of the mixed xylene fraction obtained by solvent extraction and fractional distillation of petroleum reformates, its principal source is by manufacture from benzene and ethylene.

7.5.2 PHYSICAL PROPERTIES

Many of the properties of the individual C_8 aromatic isomers are very similar. A consequence of this is that the production of individual components of very high purity becomes difficult. Since there is a great demand for ortho- and para-xylene, a great deal of research effort has been directed to accomplishing separation of these isomers. A consequence of this is that a large amount of physical and chemical data is available for these isomers. Table 7-6 presents physical and thermodynamic data for the individual C_8 isomers (9).

The distillation characteristics of these isomers are of great practical importance. While ortho-xylene can be separated readily from meta-xylene by distillation, it is only with difficulty that ethylbenzene can be distilled from para-xylene. It is not at all practical to separate para-xylene from meta-xylene by distillation. Under such



TABLE 7-6

PHYSICAL PROPERTIES OF THE
EIGHT CARBON ATOM AROMATIC ISOMERS

<u>PROPERTY</u>	<u>ETHYLBENZENE</u>	<u>p-XYLENE</u>	<u>m-XYLENE</u>	<u>o-XYLENE</u>
Density, g/cm ³				
at 20 °C	0.86702	0.86105	0.86417	0.88020
at 25 °C	0.86264	0.85669	0.85990	0.87596
Boiling Point, °C, 101.3 kPa	136.186	138.351	139.103	144.411
Freezing Point, °C	-94.975	-13.263	047.872	-25.182
Refractive Index				
n_D^{20}	1.49588	1.49582	1.49722	1.50545
n_D^{25}	1.49320	1.49325	1.49464	1.50295
Critical Temperature, °C	346.4	345.0	346.0	359.0
Critical Pressure, MPa	3.75	3.45	3.55	3.65
Critical Density, g/cm ³	0.29	0.29	0.27	0.28
Critical PV/RT	0.26	0.25	0.27	0.26
Heat of Vaporization, ΔH_v , kJ/mol				
at 25 °C	42.25	42.38	42.66	43.43
at boiling point	35.98	36.07	36.40	36.82
Heat of Fusion, ΔH_f , kJ/mol	91.63	17.11	11.57	13.60
Cryoscopic Constants ¹ , Mol				
Fraction/K				
A	0.03471	0.02509	0.02741	0.02659
B	0.0029	0.0028	0.0027	0.0030





TABLE 7-6 (cont.)

<u>PROPERTY</u>	<u>ETHYLBENZENE</u>	<u>p-XYLENE</u>	<u>m-XYLENE</u>	<u>o-XYLENE</u>
Heat of Combustion, ΔH_c , MJ/mol (25 °C to H ₂ O (liq.) ^c and CO ₂ (gas))	4.565	4.553	4.552	4.553
Heat of Formation, kJ/mol (25 °C)	-12.46	-24.43	-25.42	-24.44
Entropy, J/day. mol (25 °C)	255.10	247.36	252.17	246.48
Free energy of Formation, kJ/mol (25 °C)	33.88	31.15	30.46	31.22
C.A.S. Registry Numbers ²	100-41-4	106-42-3	108-38-3	95-47-6
Synonyms ³	Ethylbenzol Phenylethane EB	p-xylol 1,4-dimethyl- benzene p-dimethyl- benzene 1,4-xylene	m-xylol 1,3-dimethyl- benzene m-dimethyl- benzene 1,3-xylene	1,2-dimethyl- benzene o-dimethyl- benzene o-xylol 1,2-methyl- toluene

¹ For calculating purity, p , in mol %: $\log p = 2.00000 - (A/2.30259) (T_1 - T) [1 + B (T_1 - T)]$, where T is f.pt. in K of the pure component, and T is f.pt. in K of the actual sample.

² C.A.S. Registry Number for xylene is 1330-20-7.

³ Synonyms for xylene are xylol, dimethylbenzene and dilan.

circumstances, the assumption of "ideal" solutions when making distillation calculations may not be valid. Calculations of activity co-efficients at infinite dilutions based on studies of the non-ideality of the mixed xylene isomers have been made and are presented in Table 7-7, along with the corresponding vapor pressure ratios (9).

Since deviations from ideality in these systems are symmetrical, the activity co-efficient for para-xylene at infinite dilution in ethylbenzene is equal to the value for ethylbenzene at infinite dilution in para-xylene. The non-ideality can have a significant effect on the relative volatility (relative volatility is the product of the activity co-efficient multiplied by the vapor pressure ratio), particularly in the case of the ethylbenzene/para-xylene binary system. Since the number of theoretical plates in a distillation column is an exponential function of the relative volatility, the small non-ideality that exists does have a practical significance.

The relationship of vapor pressure with temperature for these compounds is presented in Table 7-8. It can be readily seen that there is very little difference between the vapor pressures of the individual C_8 isomers.

A great deal of data has been published on azeotropes of these compounds. The use of selective azeotropic distillation has been studied for separation of isomers and also for removal of non-aromatic hydrocarbons from the mixed xylenes (9). Alcohols were found to be the best class of compounds for selectively azeotroping the mixed xylenes.



TABLE 7-7ACTIVITY COEFFICIENT OF C₈ AROMATIC ISOMERS

<u>ISOMER</u>	<u>ACTIVITY COEFFICIENT¹ AT INFINITE DILUTION</u>	<u>VAPOR PRESSURE RATIO</u>
Ethylbenzene/p-xylene	1.0072	1.060
Ethylbenzene/m-xylene	1.0083	1.081
Ethylbenzene/o-xylene	1.0081	1.241
p-xylene/m-xylene	1.0007	1.020
p-xylene/o-xylene	1.0034	1.173
m-xylene/o-xylene	1.0049	1.151

¹ At boiling point at atmospheric pressure



TABLE 7-8

VAPOR PRESSURES OF C₈ AROMATICS

<u>VAPOR PRESSURE, kPa</u>	<u>TEMPERATURE, °C</u>			
	<u>ETHYL BENZENE</u>	<u>p-XYLENE</u>	<u>m-XYLENE</u>	<u>o-XYLENE</u>
1.333	25.88	27.32	28.24	32.14
2.666	38.60	40.15	41.07	45.13
4.000	46.69	48.31	49.23	53.38
5.333	52.75	54.42	55.33	59.56
6.666	57.66	59.36	60.27	64.56
7.999	61.79	63.54	64.44	68.78
10.666	68.60	70.38	71.28	75.70
13.332	74.11	75.93	76.82	81.31
19.998	84.69	86.58	87.45	92.09
26.664	92.68	94.63	95.48	100.22
33.331	99.18	101.17	102.01	106.83
40.000	104.70	106.72	107.55	112.44
53.329	113.82	115.89	116.70	121.71
66.661	121.27	123.37	124.16	129.27
79.993	127.60	129.73	130.51	135.70
93.326	133.15	135.30	136.07	141.33
106.658	138.11	140.28	141.03	146.36
119.990	142.60	144.79	145.52	150.91
133.322	146.71	148.91	149.63	155.08
159.987	154.06	156.29	156.98	162.53
199.984	163.47	165.73	166.39	172.07



7.5.3 CHEMICAL PROPERTIES

Chemical reactions of the C_8 aromatic compounds can be divided into three categories: reactions involving the number and position of the alkyl groups; chemical reactions of the alkyl groups; reactions involving the aromatic ring. The first category is of primary interest in the production of pure individual isomers. The second category includes the transformation of the pure isomers into products of commercial interest. The third category is mainly electrophilic substitution, which these compounds undergo more readily than benzene or toluene because of the activating effect of the alkyl groups.

7.5.3.1 REACTIONS INVOLVING THE ALKYL GROUPS

7.5.3.1.1 ISOMERIZATION

Experimental studies of the isomerization of xylenes in the liquid phase using various halide catalysts at 50-120 °C, gave no ethylbenzene in the products. The meta-isomer was found to be in a higher concentration than expected from its equilibrium concentration. This effect may be influenced by the concentration of the catalyst (9).

In the presence of large amounts of BF_3 , the xylenes form a complex and remain in the acid phase. In the protonated form, xylenes isomerize almost exclusively to the configuration which gives the most basic structure, the meta-isomer.

Vapor-phase isomerization of m-xylene with different catalysts has been studied at temperatures above 380 °C. At 1.317 MPa with Pt on silica-alumina catalyst, an equilibrium mixture of xylenes is obtained

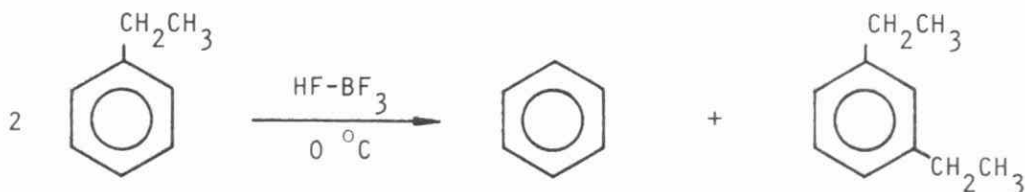


from meta-xylene; no ethylbenzene is produced. At low pressure (10.13-101.32 kPa) with a silica-alumina catalyst, a small conversion of meta-xylene to ethylbenzene occurs. At high pressures (4.05 MPa) with tungsten-molybdenum on silica-alumina catalyst, the presence of ethylbenzene adversely affects the extent of xylene isomerization. The isomerization of ethylbenzene to xylenes does not occur readily.

The mechanism of xylene isomerization is believed to be of an intramolecular nature. Addition of a proton to the aromatic to form a carbonium ion is the first step. On rearrangement and subsequent elimination of the proton the isomerized product results. Also, the isomerization of ethylbenzene may occur through formation of hydrogenated intermediates which are later dehydrogenated to xylenes.

7.5.3.1.2 DISPROPORTIONATION

Disproportionation of ethylbenzene and meta-xylene occurs with an HF-BF_3 catalyst. The disproportionation is a function of BF_3 concentration up to an equimolar ratio of the BF_3 to aromatic. The migration of ethyl groups is much faster than that of methyl groups (9). In the presence of excess HF-BF_3 , almost complete disproportionation of ethylbenzene occurs at 0 °C.



At 66 °C, meta-xylene is unreactive, but at higher temperatures it disproportionates.

7.5.3.1.3 DEALKYLATION

Dealkylation reactions, involving xylenes in the presence of hydrogen, result in many higher molecular weight products, including bicyclic and polycyclic products.

Studies of the dealkylation of xylenes in the presence of hydrogen, show that the reaction is principally thermal, that pressure has little effect on the degree of conversion, and that the xylene reaction products are formed by two consecutive reactions



Dealkylation of ethylbenzene under similar conditions is more complex. At least three reactions occur:



The production of styrene has only been observed in reactions carried out below 2.03 MPa pressure. The complexity of these reactions makes a kinetic analysis difficult. The dealkylation rate of ethylbenzene under these conditions appears to be slightly greater than for the xylenes.

7.5.3.1.4 OTHER REACTIONS OF THE ALKYL GROUPS

The most important reactions of the C₈ aromatic isomers from a



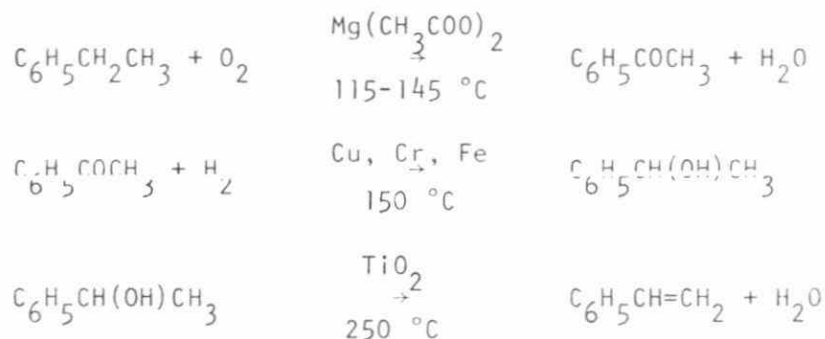
commercial view point, are oxidation of the methyl groups and dehydrogenation of the ethyl group.

Ethylbenzene is catalytically dehydrogenated to give styrene and hydrogen.



High temperatures and low pressure favor the dehydrogenation.

Ethylbenzene can also be reacted by oxidative dehydrogenation to give styrene.

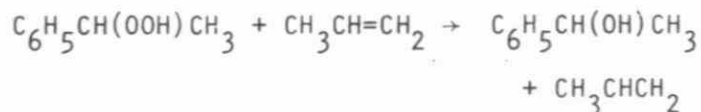


The principal intermediates are acetophenone and α -phenylethyl alcohol, with some phenylethyl alcohol and organic acids being formed in the oxidation step.

A second oxidative dehydrogenation process for conversion of ethylbenzene to styrene involves the production of the hydroperoxide.

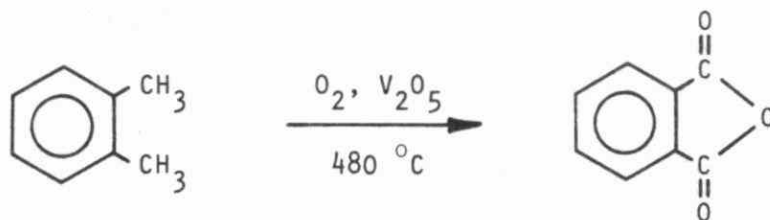


This product is then reacted with propylene to form propylene oxide and α -phenylethyl alcohol.

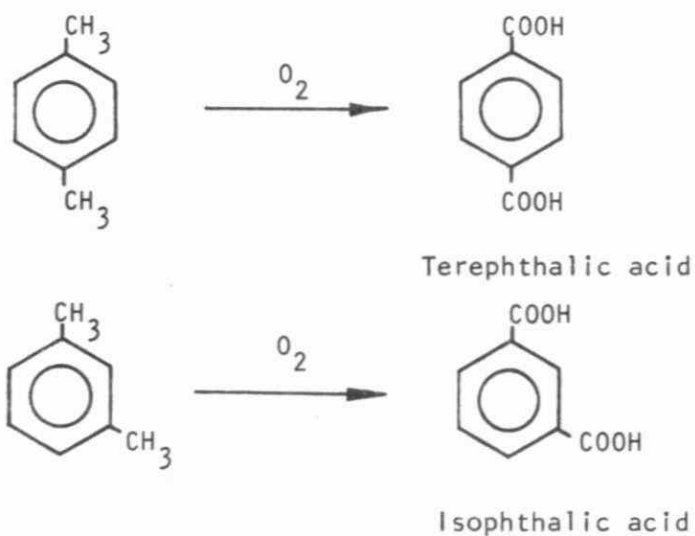


The α -phenylethyl alcohol is then dehydrated to styrene as above.

Oxidations of the xylenes are generally performed on the pure isomers.

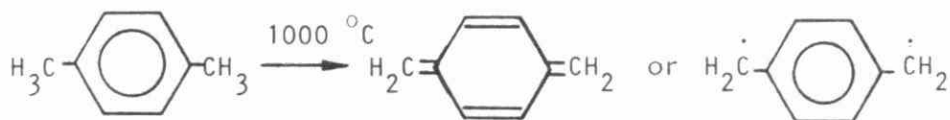


The principal products are phthalic acids or derivatives.

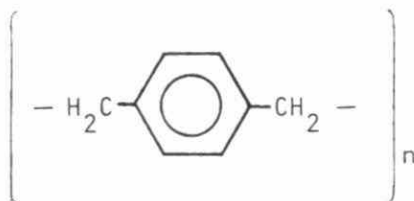


These phthalic acids and derivatives are used commercially in the production of polyesters and plasticizers.

Pyrolysis of xylenes may lead to interesting products. Para-xylene forms para-xylylene, $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$, when subjected to temperatures above 1000°C . The product is a precursor of a class of hydrocarbons known as Chichababin hydrocarbons. These compounds may be represented either by a quinonoid structure (I) or by a benzenoid biradical structure (II).



Condensation of the gaseous products from this reaction leads to the production of a very stable polymer:

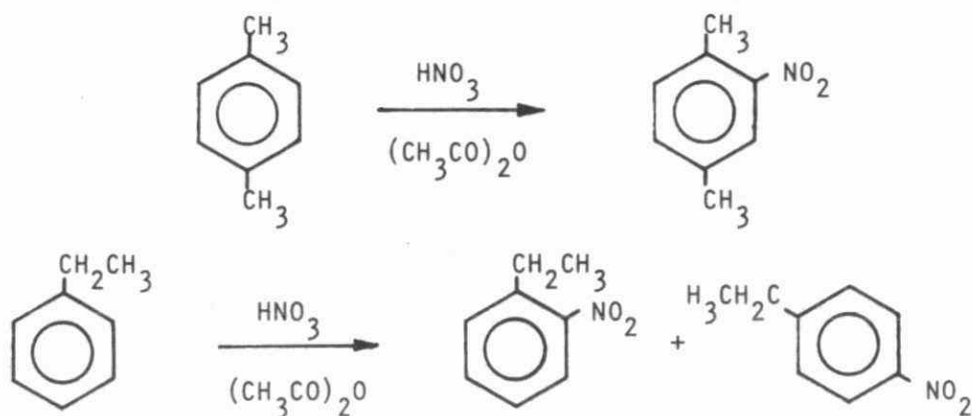


7.5.3.2 REACTIONS OF THE AROMATIC RING

The xylenes and ethylbenzene undergo the same electrophilic substitution reactions as benzene and toluene, but under milder conditions. This is because of the activating effect of the extra methyl group.

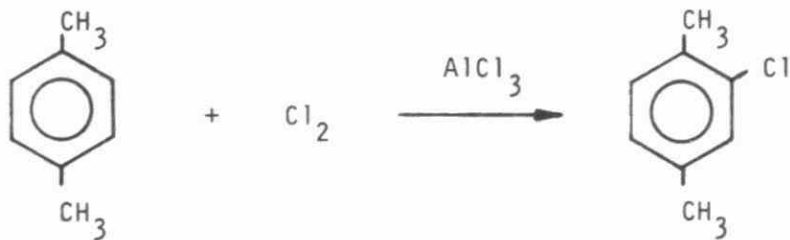
7.5.3.2.1 NITRATION

The xylenes can be nitrated under milder conditions than both benzene and toluene.



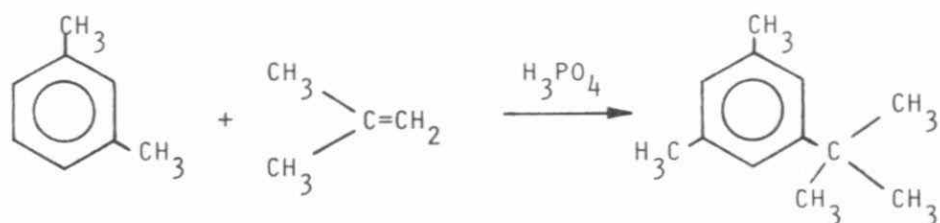
7.5.3.2.2 CHLORINATION

The nuclear chlorination of various methyl benzenes in acetic acid has been studied both with and without catalysts (9). The rates of reaction relative to benzene are very large for the xylene isomers.



7.5.3.2.3 ALKYLATION

A wide range of catalysts, promoters and alkylating agents have been employed in this reaction. By far the most common catalysts used are aluminium chloride or strong mineral acids.

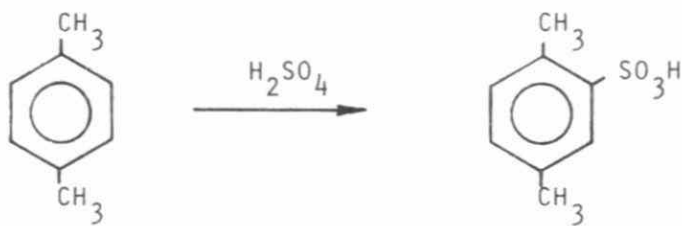


Over fifty alkylation reactions of the four C_8 aromatic isomers have been summarized (9).

7.5.3.2.4 SULFONATION

Aromatics are readily sulfonated by sulfuric acid, sulfur trioxide, or oleum. The reaction is reversible.

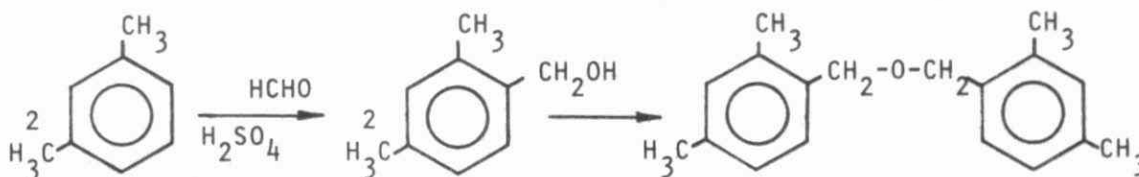
Extensive studies of the sulfonation of various methylbenzenes have been carried out (9). Under the experimental conditions employed, the aromatics reacted completely to give the mono-sulfonic acids. The reaction rate was found to be first order in the aromatic concentration.



7.5.3.2.5 FORMALDEHYDE REACTIONS

The three xylene isomers can be reacted with formaldehyde to form resins either separately or in admixture. Meta-xylene, however, is the kinetically favoured isomer.

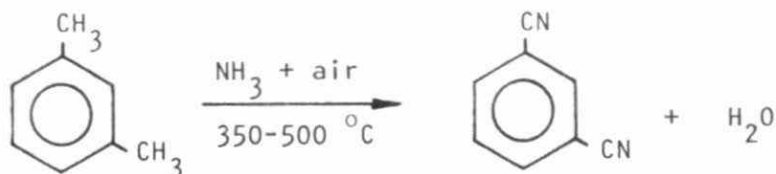
The reaction proceeds by protonation of formaldehyde to give a carbonium ion, $(\text{CH}_2\text{OH})^+$. This intermediate in turn adds to xylene with the regeneration of a proton. The aromatic product from this reaction can further react with itself or with more aromatic or with more formaldehyde. Dehydration may occur, depending on the severity of the reaction conditions. The products are mixtures of polymers of hydrocarbons, ethers, acetals, and polyacetals. The polymers are of relatively low molecular weight (around 1000). The formation of a simple ether is illustrated.



7.5.3.2.6 REACTION WITH AMMONIA

The production of aromatic nitriles directly from the corresponding alkylbenzenes by reaction with ammonia has been studied. It is a vapor phase reaction at high temperatures and requires a contact catalyst.





Para-xylene gives terephthalonitrile, the expected product, as the main product. Some p-tolunitrile ($\text{CH}_3\text{C}_6\text{H}_4\text{CN}$) is formed at first, and there is some formation of CO_2 and HCN . The maximum yield of terephthalonitrile is 89 %. Meta-xylene gives iso-phthalonitrile and ortho-xylene a mixture of phthalonitrile and phthalimide. Each xylene reacts the same whether alone or in admixture with its isomers.

7.5.3.3 COMPLEX FORMATION

The xylene isomers have been reported to form clathrate compounds. Schaeffer and co-workers (9) have reported that metal salt complexes of substituted pyridines are a class of clathrate formers that are effective in separating aromatic isomers including xylene isomers. These workers also discussed ways of making these complexes and recovering guest compounds from them.

Aromatic hydrocarbons are capable of forming complexes with a wide variety of electrophilic agents. These complexes, particularly between C_8 aromatic isomers and HF-BF_3 , are important in that they can affect the



course of reactions such as alkylation, by causing other side reactions which affects the overall product distribution. An example of this is, where an excess of catalyst is present during an alkylation reaction, the C_8 isomers form a complex and remain in the acid phase. In the protonated form, the xylenes isomerize almost exclusively to the configuration that gives the most basic structure, the meta isomer.



7.6 CUMENE

7.6.1 INTRODUCTION

Cumene ($C_6H_5CH(CH_3)_2$) is a member of the alkyl aromatic family of hydrocarbons after toluene and ethylbenzene. It is isomeric with several other compounds, such as normal propylbenzene, the ethyltoluenes, and the trimethylbenzenes. Cumene is a clear, colorless, refractive, volatile liquid with a characteristic aromatic odor.

Cumene is a naturally occurring substance present in many crude oils. However, the chief source of cumene is by manufacture from benzene and propylene. The major use of cumene is in the manufacture of phenol and acetone, and to a lesser degree as a component of motor fuels, particularly aviation gasoline.

7.6.2 PHYSICAL PROPERTIES

Some physical and thermodynamic properties of cumene are listed in Table 7-9 (10). The solubility of cumene in water is reported as 50 mg/l at 25 °C (7). Cumene is soluble in many organic solvents. The relationship of vapor pressure with temperature for cumene is presented in Table 7-10. The vapor pressure of cumene at ambient temperature (25 °C) is 613.28 Pa. However, recent calculations by MacKay and Wolkoff (7) indicate that although cumene has a low vapor pressure, its evaporation rate from water is quite high, because of its very high activity coefficient in water. They calculated a half-life for cumene evaporation from water of 1 metre depth to be 14.2 min. This factor is of importance in sampling and analysis of cumene pollution. These workers also calculated that 92 % of the cumene originally present



TABLE 7-9

PHYSICAL PROPERTIES OF CUMENE

Molecular Formula	$C_6H_5CH(CH_3)_2$
Physical State	Liquid
Freezing Point, °C	-96.033
Boiling Point, °C	152.392
Density, g/cm ³	
0 °C	0.8786
20 °C	0.8618
40 °C	0.8450
Refractive Index, n_D^{20}	1.49145
Specific Heat (liquid) at 25 °C, J/g. °C	1.544
Thermal Conductivity, W/m °C	4.477
Flash Point (closed cup), °C	35
Viscosity, mPa.sec	
0 °C	1.076
20 °C	0.791
40 °C	0.612
Surface Tension at 20 °C, mN/m	0.282
Critical Temperature, °C	351.4
Critical Pressure, MPa	2.786
Critical Density, g/cm ³	0.28
Heat of Vaporization at b.pt, J/g	312.13
Heat of Formation at 25 °C, kJ/mol	-41.20
Entropy at 25 °C, J/mol. °C	279.78
Free Energy at 25 °C, kJ/mol. °C	124.3
Heat of Combustion at Const. pressure, kJ/g	
gross	49.93
net	41.20
Cryoscopic Constant, A	0.028
B	0.003



TABLE 7-9 (cont.)

C.A.S. Registry Number

98-82-8

Synonyms

Cumol

Isopropylbenzene

2-phenylpropane



TABLE 7-10
VAPOR PRESSURE-TEMPERATURE RELATIONSHIP
FOR CUMENE

<u>PRESSURE, KPa</u>	<u>TEMPERATURE, °C</u>
1.333	38.29
6.666	71.12
13.332	88.13
26.664	107.35
53.329	129.23
79.993	143.50
101.325 (Atm. pressure)	152.39
106.658	154.38
133.322	163.30
199.984	180.67

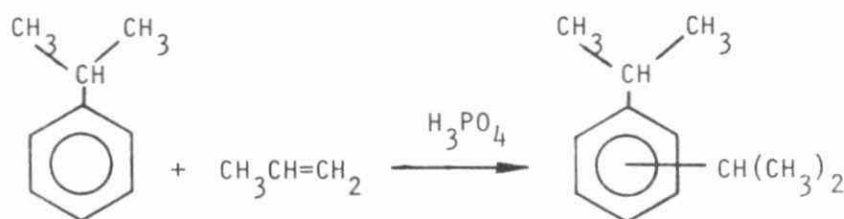


in the water is evaporated when only 0.01 % of the water had evaporated. As these figures are obtained from theoretical calculations they contain a large degree of uncertainty, but must certainly be considered during sampling and analysis of water.

7.6.3 CHEMICAL PROPERTIES

Cumene undergoes all of the normal substitution and addition reactions of alkylbenzenes. It substitutes under milder conditions than benzene because of the activating effect of the isopropyl group on the aromatic ring. However, the para-substitution product is favored because of the steric effect of the isopropyl group on the ortho-ring positions.

The only substitution reaction of cumene of commercial interest is alkylation to diisopropylbenzenes with propylene.

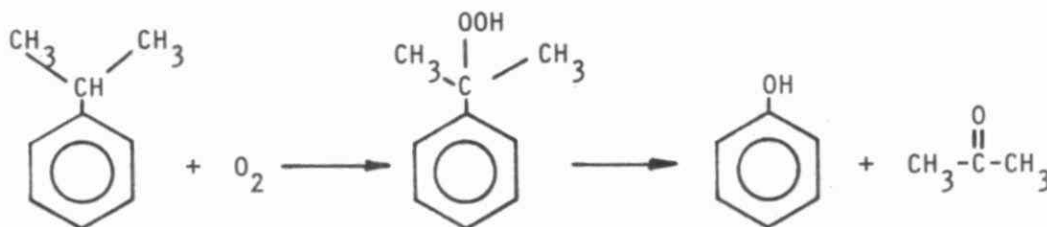


A mixture of isomers is obtained, with the para-diisopropylbenzene isomer being the main product. This isomer is separated from the other diisopropylbenzene isomers by fractional distillation, and can be oxidized to terephthalic acid. Thus, para-diisopropylbenzene is sometimes used as a substitute raw material for para-xylene in the



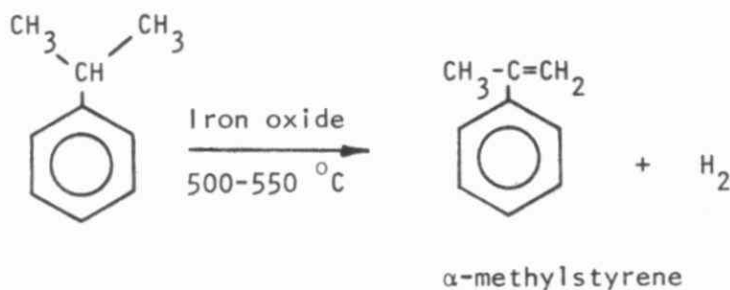
synthesis of terephthalic acid, an important intermediate in polyester fibre manufacture.

Two of the sidechain reactions of cumene are of commercial interest. The one of greatest importance is oxidation to cumene hydroperoxide which is used industrially to manufacture phenol and acetone.



Cumene hydroperoxide is also used as a chain initiator in polymer chemistry.

The other sidechain reaction of cumene of importance is dehydrogenation to form α -methylstyrene.



α -methylstyrene is also formed as a by-product in the manufacture of phenol and acetone by the cumene oxidation process (about 1.7 % by volume). α -methylstyrene is used widely in polymer formulations for modified polyesters and alkyds. Low molecular weight α -methylstyrene polymers are viscous liquids that are used as plasticizers in paints, waxes, adhesives and plastics.



7.7 STYRENE

7.7.1 INTRODUCTION

Styrene ($C_6H_5CH=CH_2$) is the common name for the simplest and most important member of a series of unsaturated aromatic monomers. It is a clear, colorless, refractive liquid with a characteristic odor. Styrene is used almost exclusively for the manufacture of polymers, including polystyrene, acrylonitrile-butadiene-styrene terpolymer, styrene-acrylonitrile copolymer, and for the production of styrene-butadiene synthetic rubber.

Styrene was first isolated in the nineteenth century from the distillation of storax, a natural balsam. Use of styrene as a monomer for polymerization products did not become commercially feasible until after the development of a process in the 1930's to manufacture high purity styrene by dehydrogenation of ethylbenzene.

7.7.2 PHYSICAL PROPERTIES

The physical properties of styrene are listed in Table 7-11 (11). The solubility of styrene in water is 0.03 % by weight at 20 °C. Styrene is soluble in many organic solvents. Its evaporation rate from water (butyl acetate = 1) is 0.49.

Table 7-12 presents the vapor pressure-temperature relationship for styrene.

7.7.3 CHEMICAL PROPERTIES

The only reactions of styrene that are of commercial significance are polymerization and copolymerization. Almost all of the styrene manufactured is used in these processes.



TABLE 7-11

PHYSICAL PROPERTIES OF STYRENE

Molecular Formula	$C_6H_5CH=CH_2$
Physical State	Liquid
Boiling Point at 101.3 kPa, °C	145.0
Freezing Point, °C	-30.6
Flashpoint, °C	
Tag Open-cup	34.4
Cleveland Open-cup	31.1
Fire Point, °C	
Tag Open-cup	34.4
Cleveland Open-cup	34.4
Autoignition Temperature, °C	490
Explosive Limits in Air, %	1.1 - 6.1
Vapor Pressure at 25 °C, kPa	0.823 ¹
Vapor Density (air = 1)	3.6
Critical Pressure, MPa	3.81
Critical Temperature, °C	369.0
Critical Density, g/cm ³	0.282
Refractive Index, n_D	
at 15 °C	1.5495
20 °C	1.5467
25 °C	1.5439
30 °C	1.5410
35 °C	1.5382
Viscosity, mPa.s	
0 °C	1.040
20 °C	0.763
40 °C	0.586
60 °C	0.470
80 °C	0.385
100 °C	0.326
120 °C	0.278
140 °C	0.243



TABLE 7-11 (cont.)

Surface Tension, mN/m	
0 °C	31.80
20 °C	30.86
40 °C	29.93
60 °C	29.01
80 °C	28.08
100 °C	27.15
120 °C	26.23
140 °C	25.30
Density, g/cm ³	
0 °C	0.9237
10 °C	0.9148
20 °C	0.9050
30 °C	0.8970
40 °C	0.8880
60 °C	0.8702
80 °C	0.8524
100 °C	0.8346
150 °C	0.7900
Specific Heat, liquid, J/g. °C	
0 °C	1.636
20 °C	1.690
40 °C	1.748
60 °C	1.811
80 °C	1.887
100 °C	1.983
120 °C	2.104
140 °C	2.238
Specific Heat, vapor, at 25 °C, C _p , J/g. °C	1.179
Latent Heat of Vaporization, ΔH_v , J/g	
at 25 °C	428.4
at 145 °C	354.3
Heat of Combustion, gas, at const. Pressure, at 25 °C, ΔH_c , kJ/mol	4262.8
Heat of Formation, liquid, at 25 °C, ΔH_f , kJ/mol	147.36
Heat of Polymerization, kJ/mol	74.48
Volumetric Shrinkage upon polymerization, %	17.0



TABLE 7-11 (cont.)

Solubility at 25 °C, %	
Styrene in water	0.032
Water in styrene	0.070
C.A.S. Registry Number	100-42-5
Synonyms:	Cinnamene Phenethylene Phenylethane Phenylethylene Styrol Styrolene Vinylbenzene Vinylbenzol



TABLE 7-12
VAPOR PRESSURE-TEMPERATURE RELATIONSHIP
FOR STYRENE

<u>TEMPERATURE, °C</u>	<u>VAPOR PRESSURE, kPa¹</u>
0	0.151
10	0.312
20	0.604
30	1.108
40	1.934
50	3.235
60	5.208
80	12.230
100	25.720
120	49.419
140	88.116
145	101.325

¹ Calculated from the Antoine Equation,

$$\log_{10} p = 6.95711 - \frac{1445.58}{209.43 + k \text{ } ^\circ\text{C}}$$

p obtained in mm Hg; 1 mm Hg = 133.324 Pa.



Styrene monomer can be polymerized by all of the common methods used in plastics technology. Techniques of mass, suspension, solution and emulsion polymerization have been used for the manufacture of polystyrene and styrene copolymers, but processes employing the first two methods account for most of the polymer manufacture. A free-radical polymerization of the monomer initiated thermally or with catalysts is generally employed.

In addition to polymerization, styrene also undergoes all of the normal reactions of a typical unsaturated compound. These include addition reactions across the double bond such as halogenation, hydrogenation, hydrohalogenation, hydration and hydrosulfonation to give side-chain-substituted ethylbenzenes, oxidation reactions such as ozonization to form benzaldehyde, hydroxylation to form phenyldiols, and alkylation to form higher alkylbenzenes. Most of these reactions are only of academic interest.



7.8 NAPHTHALENE

7.8.1 INTRODUCTION

Naphthalene, $C_{10}H_8$, is an aromatic hydrocarbon with two ortho-condensed benzene rings. It is the first member of the series of condensed-ring aromatic compounds. It is a white, easily sublimable, crystalline solid with, in pure form, a mild, pleasant, characteristic odor. It burns in air with the formation of soot.

The principal use of naphthalene is as a raw material in the production of phthalic anhydride and a large number of intermediates for synthetic organic dyes, insecticides, plasticizers and pharmaceuticals, as well as in the production of the solvents tetra- and decahydronaphthalene. It is also used as an insecticide, principally for clothes moths.

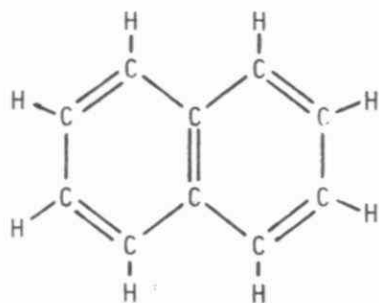
Naphthalene was first discovered by Garden in 1820, who isolated the compound as a solid from coal tar distillates. It was called naphthalene in 1821 by Kidd who isolated the compound in purer form from pyrolyzed coal tar. Erlenmeyer in 1866 demonstrated that naphthalene was a hydrocarbon with two benzene nuclei condensed in the ortho position, and Graeble in 1869 established the accepted structural formula by its oxidation to orthophthalic acid.

7.8.2 PHYSICAL PROPERTIES

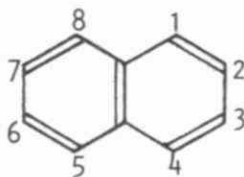
7.8.2.1 STRUCTURE

Naphthalene is the first member in the series of aromatic compounds with condensed rings. The formula I is usually abbreviated to II or III. The preferred numbering of the molecule is shown in II.

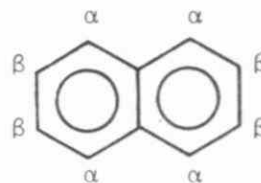




(I)

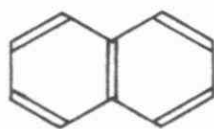


(II)

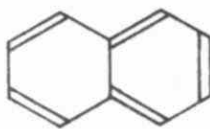


(III)

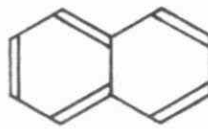
However, positions 1, 4, 5 and 8 are often designated as α (alpha) and positions 2, 3, 6 and 7 as β (beta) (shown in III). Formula III is now the preferred notation. The configuration of the naphthalene molecule cannot be represented by one definite structure. According to resonance theory, the three structures IV, V and VI all make approximately equal contributions.



(IV)



(V)



(VI)

However, it can be seen that only in IV are both rings aromatic; in V and VI one ring is aromatic and the other has a cyclohexadiene structure. Almost all chemical reactions of naphthalene and its derivatives proceed according to IV as if the double bonds were "frozen"



in these positions.

7.8.2.2 PHYSICAL CONSTANTS

Table 7-13 shows some physical properties of naphthalene (12). Naphthalene is only slightly soluble in water (0.019 g/l at 0 °C and 0.030 g/l at 100 °C) but is soluble in many organic solvents. The best solvent for naphthalene is tetrahydronaphthalene, which has the greatest configurational similarity to naphthalene. Naphthalene is also soluble in liquid sulfur dioxide (imparting a greenish yellow color) and in phenols, ethers, acetic acid, fats and volatile oils. Naphthalene is a good solvent for many compounds including inorganic substances such as phosphorus, iodine, sulfur, and several metal sulfides.

The vapor pressure-temperature relationship for naphthalene is presented in Table 7-14 (12). The vapor pressure at ambient temperatures is very low compared to other aromatic hydrocarbons.

Naphthalene forms azeotropes with various compounds, and several examples are presented in Table 7-15 (12).

7.8.3 CHEMICAL PROPERTIES

Naphthalene derivatives are important intermediates in the manufacture of such products as dyes, pharmaceuticals, agricultural chemicals, and surface-active agents. The reactions of naphthalene are of three distinct types, ie substitution, addition and rupture of one or both of the rings.



TABLE 7-13

PHYSICAL PROPERTIES OF NAPHTHALENE

Formula	$C_{10}H_8$
Physical State	Solid
Melting Point, °C	80.290
Boiling Point, °C	217.955
Density, g/cm ³	
d_4^{20}	1.01813
d_4^{85}	0.9752
Refractive Index, n_D^{25} at 85 °C	1.5898
Flash Point (closed cup), °C	79
Ignition Temperature, °C	526
Flammable Limits, vol % in air	0.9 - 5.9
Heat of Fusion, kJ/mol	18.98
Free Energy of Formation at 25 °C, (solid), kJ/mol	19.84
Heat of Formation at 25 °C, kJ/mol	
solid	78.45
liquid	96.32
gaseous	151.70
C.A.S. Registry Number	91-20-3
Synonyms	Naphthalin Naphthaline Naphthene Tar Camphor White Tar Moth Flakes



TABLE 7-14
VAPOR PRESSURE-TEMPERATURE RELATIONSHIP
FOR NAPHTHALENE

<u>TEMPERATURE, °C</u>	<u>VAPOR PRESSURE, kPa</u>
0.0	0.0008
10.0	0.0028
20.0	0.0072
40.0	0.0427
87.6	1.333
119.1	5.33
166.3	26.66
191.3	53.33
214.3	93.33
218.0	101.32
230.5	133.32
250.6	200.0



TABLE 7-15

BINARY AZEOTROPES FOR NAPHTHALENE

<u>COMPOUND</u>	<u>BOILING POINT, °C</u>	<u>NAPHTHALENE, Wt %</u>
Benzoic Acid	217.70	95.0
1,2-benzenediol (catechol)	217.45	88.5
4-chlorophenol	216.30	63.5
2-nitrophenol	215.75	40.0
1,3,5-triethylbenzene	215.00	15.0
Benzyl acetate	214.65	28.0
Benzyl alcohol	204.10	40.0
m-cresol	202.08	97.2
Acetamide	199.55	72.8
Ethylene glycol	183.90	49.0



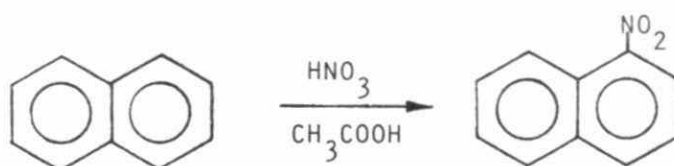
7.8.3.1 SUBSTITUTION REACTIONS

Naphthalene substitution reactions which are of industrial importance are nitration, hydroxylation, sulfonation, amination, alkylation and chlorination. Reactions at lower temperatures tend towards 1-substitution products, while at higher temperatures, 2-substitution is favored.

Although naphthalene resembles benzene in its chemical reactions in many ways, naphthalene is more reactive than benzene in both substitution and addition reactions. This is expected, theoretically, because quantum mechanical calculations show that the loss of stabilization energy for the first step in electrophilic substitution or addition decreases from benzene to naphthalene; thus the reactivity in these reactions should increase from benzene to naphthalene.

7.8.3.1.1 NITRATION

Naphthalene reacts easily with nitric acid, and mono- and polynitronaphthalenes are readily formed. Naphthalene is sufficiently reactive to be nitrated by nitric acid in acetic acid.

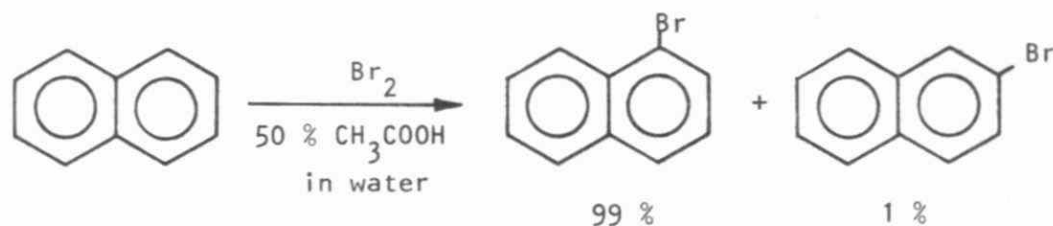


Reaction of naphthalene with a mixture of concentrated nitric acid and 80 % sulfuric acid yields 1-nitronaphthalene and only small amounts of 2-nitronaphthalene. The latter has to be prepared by indirect methods. Reduction of 1-nitronaphthalene gives 1-naphthylamine, an important intermediate for organic dyes.

7.8.3.1.2 HALOGENATION

Substitution of naphthalene by halogens takes place in the presence of a catalyst such as ferric chloride. All of the hydrogen atoms of the naphthalene molecule can be replaced. Chlorination of naphthalene dissolved in chlorobenzene yields 1-chloronaphthalene, and in carbon tetrachloride solution, 1,4- and 1,5-dichloronaphthalene are formed. Chlorination of molten naphthalene gives polychloronaphthalenes up to octachloronaphthalene. Hexa-, hepta- and octachloronaphthalenes are commercially important, because they are nonflammable waxy substances with high melting points and high dielectric constants.

Bromination of naphthalene proceeds readily in 50 % aqueous acetic acid solution.



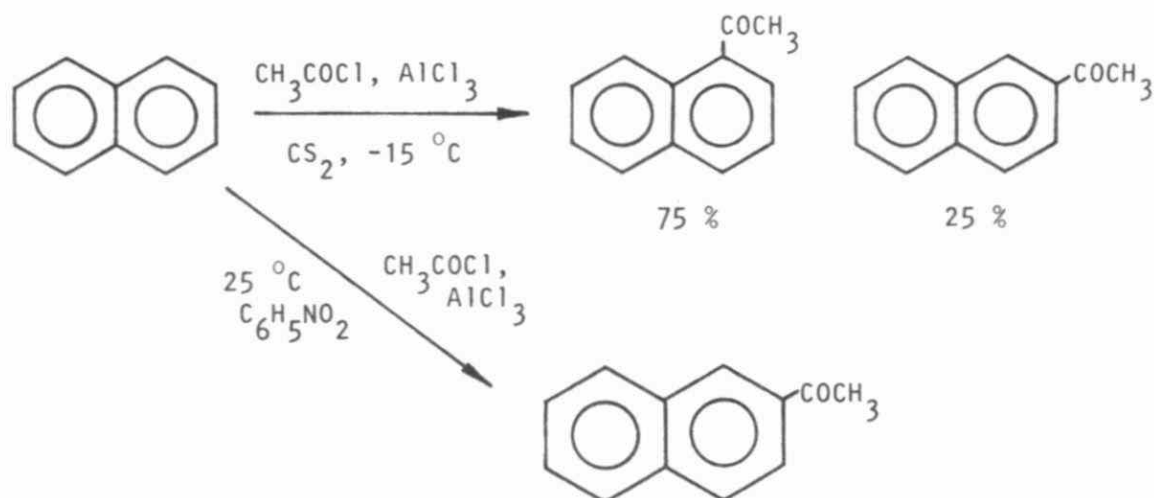
7.8.3.1.3 ALKYLATION

The alkylation of naphthalene proceeds readily with many kinds of alkylating agents in the presence of various catalysts, for example sulfuric acid, aluminium chloride and other metal halides, hydrofluoric acid and phosphoric acid. Aluminium chloride is the most active catalyst, but it forms a complex with alcohols and must then be used in large excess. A reactive alkylating agent should be used because naphthalene alone reacts to form dinaphthyls in the presence of aluminium chloride and these will be formed if the alkylating agent is of low reactivity. Reactions with aluminium chloride are usually accompanied by formation of resinous by-products, but other catalysts such as sulfuric or hydrofluoric acid give good products almost free of resinous material. Sulfuric acid is the preferred catalyst for alkylations with alcohols. If acid of sufficient strength is used alkylation and sulfonation take place simultaneously and alkylnaphthalene-sulfonic acids are formed. This method is used commercially on a large scale in the manufacture of detergents.

7.8.3.1.4 ACYLATION

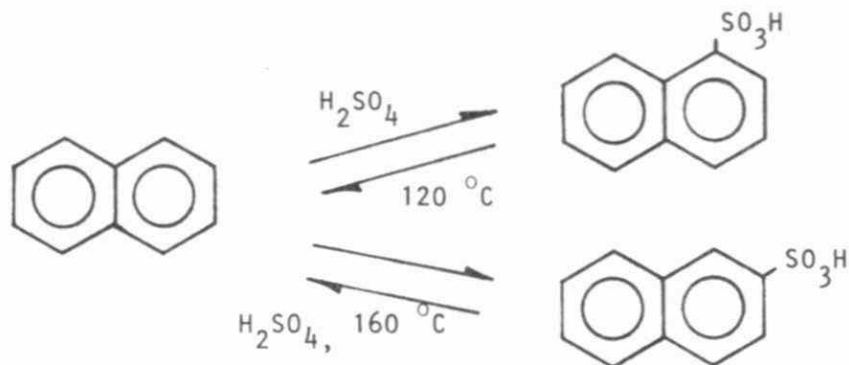
Naphthalene reacts with acid chlorides or anhydrides, in the presence of anhydrous aluminium chloride, to produce alkylnaphthylketones. However, the position of substitution is strongly dependent on the solvent. Reactions carried out in carbon disulphide produce predominantly the 1-substituent, whereas using nitrobenzene as solvent favors formation of the 2-substituent.





7.8.3.1.5 SULFONATION

Substitution of a ring hydrogen with a sulfonic acid (SO_3H) group is usually carried out by heating naphthalene with a slight excess of concentrated sulfuric acid. However, sulfonation is a reversible reaction and, in the case of naphthalene sulfonation, produces an interesting phenomenon. Naphthalene sulfonates most readily at the 1-position because of kinetic control. However, at temperatures above 160°C or with prolonged reaction times, the initial product rearranges to 2-naphthalenesulfonic acid, which is the more stable product.

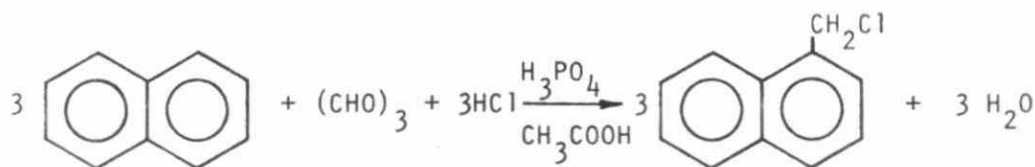


Naphthalenepolysulfonic acids (di-, tri-, and tetra-) are obtained by using sufficient fuming sulfuric acid, containing up to 70 % sulfur trioxide.

The naphthalenesulfonic acids are used as intermediates for synthetic organic dyes. Alkyl naphthalenesulfonic acids are used for making synthetic detergents, wetting agents, and emulsifiers.

7.8.3.1.6 CHLOROMETHYLATION

Naphthalene, in a mixture of glacial acetic acid and syrupy phosphoric acid, reacts with paraformaldehyde and concentrated hydrochloric acid to form 1-chloromethylnaphthalene.



7.8.3.2 ADDITION REACTIONS

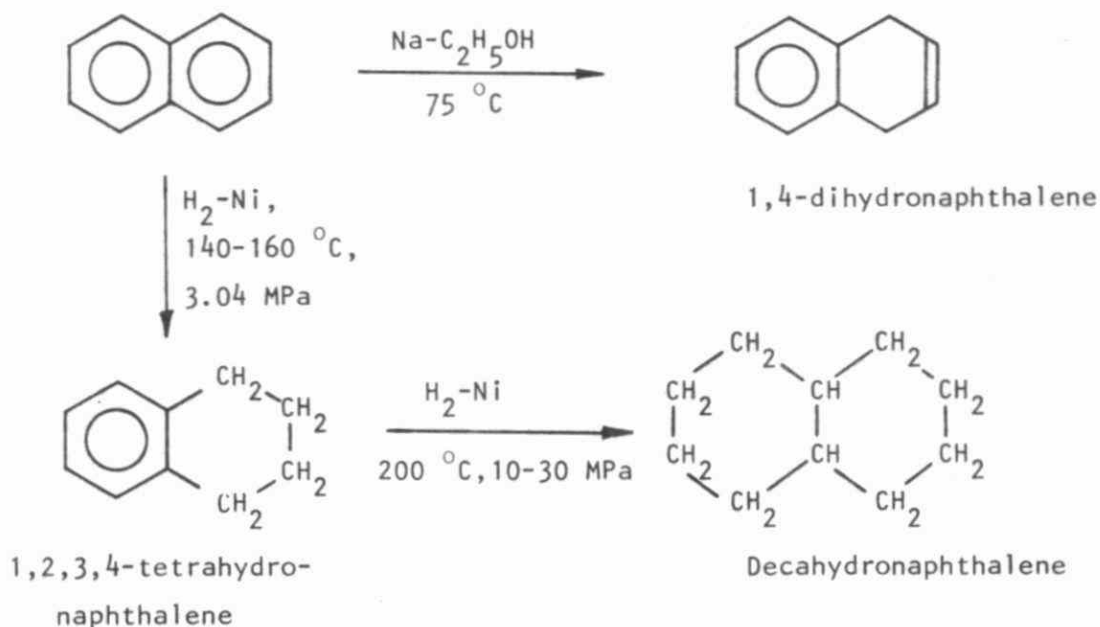
7.8.3.2.1 HYDROGENATION

Naphthalene forms di-, tetra-, hexa-, octa-, and decahydronaphthalenes. Of these only tetra- and decahydronaphthalene are of commercial importance, and are used as solvents.

Reactions of naphthalene with sodium in alcohol produces 1,4-dihydronaphthalene. Catalytic hydrogenation gives 1,2,3,4-tetrahydronaphthalene.



Further reduction to decahydronaphthalene requires prolonged catalytic hydrogenation at relatively high temperatures and pressures.



1,2-dihydronaphthalene can be prepared by reduction with sodium in ethanol at 150 °C or by isomerization of the 1,4-isomer in a hot solution of sodium ethoxide.

1,2,3,4,6,7- and 1,2,3,5,6,7-hexahydronaphthalene has been prepared by heating 9,10-dihydroxydecahydronaphthalene in dilute sulfuric acid under pressure at 150 °C.

Various isomeric forms of octahydronaphthalene have been prepared by dehydration of 1- and 2-decahydronaphthols.

7.8.3.2.2 CHLORINE ADDITION

In the absence of catalysts, and at low temperature, chlorine reacts with naphthalene by addition to give naphthalene di- and tetrachloride.

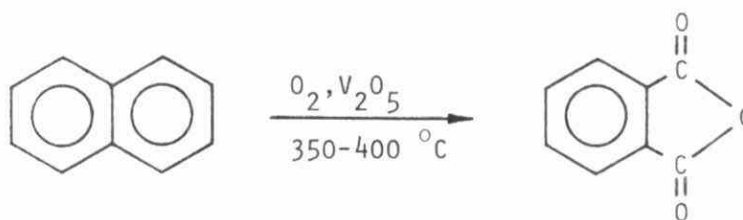
On heating, the naphthalene chlorides lose hydrogen chloride and form respectively 1-chloro- and 1,4-dichloronaphthalenes.

7.8.3.2.3 REACTIONS WITH POLYNITRO COMPOUNDS

Naphthalene forms addition compounds with polynitro compounds. The best-known example is the addition compound of naphthalene and picric acid (2,4,6-trinitrophenol). This is believed to be formed by charge transfer between the naphthalene and the picric acid.

7.8.3.3 RING RUPTURE

Oxidation of naphthalene under normal conditions leads to naphthaquinone, but if oxidation is continued beyond naphthaquinone, one ring of naphthalene ruptures with further oxidation of two carbon atoms to carbon dioxide. The two remaining carbons, ortho to each other in the ring, form carboxy groups to yield ortho-phthalic acid, which dehydrates to phthalic anhydride under the conditions of the reaction.



The production of phthalic anhydride is the largest commercial use of naphthalene.



7.9

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8 MAJOR PRODUCERS, USES AND MARKET FORECASTS



	SECTION	PAGE NO.
8	MAJOR PRODUCERS, USES AND MARKET FORECASTS	8-1
8.1	SUMMARY	8-4
8.2	INTRODUCTION	8-11
8.3	BENZENE	8-12
8.3.1	Introduction	8-12
8.3.2	Production and Sources	8-13
8.3.2.1	Production from Petroleum and Natural Gas	8-13
8.3.2.2	Canadian Production from Petroleum Sources	8-14
8.3.2.3	Benzene from Coal Carbonization	8-18
8.3.2.4	Benzene in Gasoline	8-21
8.3.3	Uses of Benzene (Extracted)	8-25
8.3.4	Market Forecast	8-30
8.4	TOLUENE	8-34
8.4.1	Introduction	8-34
8.4.2	Production and Sources	8-35
8.4.2.1	Production from Petroleum and Natural Gas	8-35
8.4.2.2	Toluene from Coal Carbonization	8-37
8.4.2.3	Toluene in Gasoline	8-41
8.4.3	Uses of Toluene	8-42
8.4.4	Market Forecast	8-48
8.5	XYLENES AND ETHYLBENZENE	8-50
8.5.1	Introduction	8-50
8.5.2	Production and Sources	8-51
8.5.2.1	Production from Petroleum	8-51
8.5.2.2	Xylenes from Coal Carbonization	8-55
8.5.2.3	Xylenes in Gasoline	8-56
8.5.3	Uses of Xylenes	8-56
8.5.4	Market Forecast	8-60
8.6	STYRENE	8-63
8.6.1	Introduction	8-63
8.6.2	Production and Sources	8-64
8.6.2.1	Production from Ethylbenzene	8-64
8.6.2.2	Styrene from Coal Carbonization	8-64
8.6.2.3	Styrene in Gasoline	8-65
8.6.3	Uses of Styrene	8-65
8.6.4	Market Forecast	8-75
8.7	CUMENE	8-79
8.7.1	Introduction	8-79
8.7.2	Production, Sources and Uses	8-79
8.7.3	Market Forecast	8-80



	SECTION	PAGE NO.
8.8	NAPHTHALENE	8-84
8.8.1	Introduction	8-84
8.8.2	Production and Sources	8-84
8.8.3	Uses of Naphthalene	8-86
8.8.4	Market Forecast	8-86
8.9	REFERENCES	8-88



8.1 SUMMARY

Available information on the production, uses, imports, and exports of selected aromatic hydrocarbons is reviewed and evaluated. In general, these data are relatively limited for most areas considered and in many cases estimates have been used because of lack of data.

For the purpose of this report all figures for production, use, export, etc. refer to the isolated or purified form of the compound of interest. This qualification is especially important where the presence of these aromatic hydrocarbons, particularly benzene, toluene and xylenes, in gasoline is discussed. The aromatic hydrocarbon content of some refinery streams used in gasoline blending is intentionally increased to improve the octane rating of the finished gasoline. Refineries in Canada produce a very large volume of gasoline (35 G1 in 1975), thus gasoline is a major source of these aromatic hydrocarbons. However, only a few of these refineries (about 10 out of a total of 60) have facilities for isolating individual aromatic hydrocarbons, normally benzene, toluene and xylenes, from their production streams. Thus, while gasoline is a major source of these hydrocarbons, gasoline blending, except where stated otherwise, is not a major use of the individual isolated aromatic hydrocarbons.

Benzene

Benzene is produced mainly from petroleum refinery processes, coking operations or by hydrodealkylation of toluene or xylene.

Crude oil contains a small amount of benzene and this is increased



by catalytic reforming (or cracking) in refinery processes to produce a reformat (or pyrolysis gasoline) which is rich in aromatics. Light oils, which are recovered from coking operations, contain significant quantities of aromatics. These are shipped to refineries for use. A major fraction of the reformat is used in blending operations for the production of gasoline. Separation of benzene, and other aromatics, from the reformat is carried out by solvent extraction followed by distillation. In the hydrodealkylation process, toluene (or sometimes xylenes) are converted to benzene and methane either catalytically or thermally. No subsequent solvent extraction is required.

Most of the benzene production in Ontario is in the Sarnia area. In 1977, the Ontario production capacity was about 200 Gg/annum (50 % of Canadian capacity). By the end of 1978 this figure should rise to 470 Gg/annum or 70 % of Canadian capacity as a result of new facilities at Petrosar's plant in Corruna and Texaco's new plant at Nanticoke.

About 80 % of light oil from coking operations in Canada is produced in Ontario (Hamilton and Sault Ste. Marie). Refineries purchase this product and blend it into their operational streams as needed.

Almost all of the benzene produced in Canada is used in the petrochemical industry. In Ontario almost all of the benzene used is reacted with ethylene to produce styrene. These operations are in Sarnia and the 1977 production capacity for styrene was about 150 Gg/annum. No cumene, cyclohexane, or maleic anhydride, etc. are manufactured in Ontario. Almost 50 % of Canadian benzene production is exported.



It is expected that Canadian production capacity for benzene will increase by 75 % by 1990 and demand will increase at an annual average rate of 8.5 % from 1976 to 1990.

A major source for benzene (in admixture with other aromatics) is due to its presence in several refinery streams used in blending operations to form gasoline. Based on an average of 1 % benzene in gasoline it can be estimated that about 310 Gg/annum of benzene was present in gasoline used during 1975 in Canada. This is at least as high as all uses of extracted benzene combined. About 110 Gg of benzene were present in gasoline used in Ontario in 1977.

Toluene

Toluene is produced mainly from petroleum refinery processes, coking operations or as a by-product of styrene production from ethylbenzene.

Crude oil contains a small amount of toluene and this is increased by catalytic reforming (or cracking) in refinery processes to produce a reformat (or pyrolysis gasoline) which is rich in aromatics. Light oils, which are recovered from coking operations, contain significant quantities of aromatics. These are shipped to refineries for use. A major fraction of the reformat is used in blending operations for the production of gasoline. Separation of toluene, and other aromatics from the reformat is carried out by solvent extraction followed by distillation. In the production of styrene from ethylbenzene, toluene is formed as a by-product, constituting 4 to 7 % of the final products.

Most of the toluene production in Ontario is in the Sarnia area. In 1977 the Ontario production capacity was about 200 Gg/annum (55 % of Canadian capacity). By the end of 1978 this figure should rise to about



340 Gg/annum or 70 % of Canadian capacity as a result of new facilities at Petrosar's plant in Corruna and Texaco's new plant at Nanticoke.

About 80 % of light oil from coking operations in Canada is produced in Ontario (Hamilton and Sault Ste. Marie). Refineries purchase this product and blend it into their operational streams as needed.

A major source for toluene (in admixture with other aromatics) is due to its presence in several refinery streams used in blending operations to form gasoline. Based on an average of 6 % toluene in gasoline it can be estimated that about 2,000 Gg/annum of toluene was present in gasoline used in Canada in 1974. About 600 Gg of toluene were present in gasoline used in Ontario in 1977.

This can be compared with all uses of extracted toluene (other than gasoline) for 1974 which total about 270 Gg/annum.

In Canada (1976), 25 % of toluene produced was blended back into gasoline blending streams, 20 % was used to manufacture benzene, 6 % was used for phenol production, 10 % for solvent use, 5 % for miscellaneous chemical production and 34 % was exported. No benzene or phenol production was carried out in Ontario.

Xylenes

Xylenes are produced from petroleum refinery processes, and coking operations.

Crude oil contains a small amount of xylene and this is increased by catalytic reforming (or cracking) in refinery processes to produce a reformat (or pyrolysis gasoline) which is rich in aromatics. Light oils, which are recovered from coking operations, contain significant



quantities of aromatics. These are shipped to refineries for use. A major fraction of the reformat is used in blending operations for the production of gasoline. Separation of xylene, and other aromatics, from the reformat is carried out by solvent extraction followed by distillation.

Most of the xylene production in Ontario is in the Sarnia area. Ontario production capacity for 1977 was about 250 Gg/annum (45 % of Canadian capacity). No separation of the o-, m- and p-xylene isomers is carried out in Ontario, however, o-xylene is used at Cornwall to produce phthalic anhydride (12 Gg/annum of o-xylene).

Although good figures are not available, it is estimated that about 90 % of xylene production in Canada is added back into gasoline blending streams or exported.

A major source of xylene (in admixture with other aromatics) is due to its presence in several refinery streams used in blending operations to form gasoline. The average concentration of xylene in gasoline is uncertain but is expected to be at least 10 %. This gives about 3,000 Gg/annum of xylene in gasoline used in 1974 in Canada or about 1,100 Gg in gasoline used in Ontario in 1977. This is by far the largest source of xylene in Canada.

Styrene

Styrene is produced in petroleum refinery operations and a small amount from coking processes in admixture with a number of other aromatics. None of this styrene is extracted for commercial use and it is used as a blending component in the production of gasoline. Although the concentration of styrene in gasoline is uncertain it may be estimated



at 0.5 %. This corresponds to about 160 Gg/annum of styrene in gasoline used in Canada during 1975 or about 60 Gg in gasoline used in Ontario in 1977.

At the present time, all styrene produced for isolated use in Canada is in the Sarnia area by dehydrogenation of ethylbenzene. Current capacity is about 200 Gg/annum. This is expected to increase to about 355 Gg/annum in 1978.

Almost all styrene production is used for polymer production such as polystyrene, styrene-butadiene rubber (SBR), styrene-butadiene latex, acrylonitrile-butadiene-styrene resins (ABS), styrene-acrylonitrile resins (SAN) and unsaturated polyesters. A very small amount of styrene is used in solvent applications (usually as a solvent for styrenic polymers - eg fiberglass).

It is estimated that market demand for styrene will grow at an average of 7 % per annum from 1976 to 1990.

Cumene

Cumene is produced by the catalytic alkylation of benzene by propylene. It is used as a feedstock for the production of phenol and acetone. There is no current production or use of cumene in Ontario.

Naphthalene

Naphthalene is produced in the coal tar fractions formed during coking operations and in the heavy reformat fractions in petroleum refinery operations. However, in Canada, recovery of naphthalene is only carried out on coal tars. The Ontario production for 1976 is estimated to be about 20 Gg/annum (80 % of Canadian capacity) with



about 15 Gg/annum being exported for phthalic anhydride production and the remainder used for miscellaneous chemical manufacture.

The average concentration of naphthalene in gasoline is not known but could range up as high as 1 %. This would correspond to 350 Gg/annum of naphthalene in gasoline in Canada for 1975 or about 120 Gg in gasoline used in Ontario in 1977.

Ethylbenzene

Ethylbenzene is produced in Ontario in Sarnia by the reaction of benzene with ethylene. The current capacity is about 200 Gg/annum and this is all used to produce styrene for polymer production. It is not known how much ethylbenzene is present in gasoline.



8.2 INTRODUCTION

In the following sections the primary producers, primary users, and secondary users of the compounds of interest are outlined. Where possible, market forecasts are also included. With the exception of the xylenes and ethylbenzene the compounds are treated independently of each other.

In cases where information was not available or was relatively limited, best estimates were made based on available data.

For the purpose of this report all figures for production, use, export, etc. refer to the isolated or purified form of the compound of interest. This qualification is especially important where the presence of these aromatic hydrocarbons, particularly benzene, toluene and xylenes, in gasoline is discussed. The aromatic hydrocarbon content of some refinery streams used in gasoline blending is intentionally increased to improve the octane rating of the finished gasoline. Refineries in Canada produce a very large volume of gasoline (35 G1 in 1975), thus gasoline is a major source of these aromatic hydrocarbons. However, only a few of these refineries (about 10 out of a total of 60) have facilities for isolating individual aromatic hydrocarbons, normally benzene, toluene and xylenes, from their production streams. Thus, while gasoline is a major source of these hydrocarbons, gasoline blending, except where stated otherwise, is not a major use of the individual isolated aromatic hydrocarbons.



8.3 BENZENE

8.3.1 INTRODUCTION

Benzene (C_6H_6) is a volatile, colorless, and flammable liquid aromatic hydrocarbon, possessing a characteristic aromatic odor. Its principal use is as a chemical raw material in the synthesis of compounds such as styrene, phenol, dodecylbenzene, nitrobenzene, cyclohexane, nonylphenol and other products used in the preparation of nonionic detergents, chlorobenzene, benzene hexachloride, and maleic anhydride. Benzene is also used as a solvent and is present in gasoline.

Benzene can be commercially produced by several methods. In the carbonization of coal, by-product coal tars may be distilled to yield various products, including a benzene fraction. Benzene is the major constituent of light oil recovered from coking operations. Petroleum feedstocks contain a small portion of benzene, and catalytic reforming of these feedstocks increases the proportion of benzene, which is recovered by solvent extraction and fractional distillation.

Prior to World War II, the amount of benzene produced by the coal carbonization industry in North America was sufficient to supply demand, even with the major portion of production being used for gasoline blending. The recovery of benzene from petroleum was not carried out commercially until about 1941. Several years after the end of World War II (about 1950) the demand for benzene (mainly for production of detergents and plastics) exceeded the total production of benzene by the coal carbonization industry. To help meet this demand, benzene was produced in ever-increasing



amounts by the petroleum industry, chiefly by the solvent extraction of petroleum reformates and by the catalytic demethylation of toluene. Since 1959, petroleum has been the major source of benzene. At the present time production of benzene from petroleum and natural gas sources accounts for over 90 % of the total benzene production in North America with the remainder from coking operations (1).

8.3.2 PRODUCTION AND SOURCES

8.3.2.1 PRODUCTION FROM PETROLEUM AND NATURAL GAS

Petroleum-derived benzene is produced commercially by two types of processes; reforming-separation processes and dealkylation processes.

In reforming-separation processes, a petroleum or natural gas condensate fraction is catalytically reformed to produce a more desirable product (higher octane number) for use in gasoline blending. Benzene and other aromatic hydrocarbons are removed from the reformed product, or a special fraction of the product, by solvent extraction, and the extracted aromatic mixture is fractionally distilled to separate benzene and other aromatic hydrocarbons (2). Benzene originally present in the petroleum fraction goes through the process unchanged. The total benzene yield includes originally present benzene and benzene formed from various precursors, primary cyclohexane and methylcyclopentane (3). The yield of benzene from these processes can vary from 2-40 % of the final product depending on the choice of boiling range of the reformat fraction subjected to solvent extraction (2, 3).



In dealkylation processes, toluene (and sometimes xylene) is hydro-dealkylated, either catalytically or thermally, to yield benzene and by-product methane; no solvent extraction being necessary.

8.3.2.2 CANADIAN PRODUCTION FROM PETROLEUM SOURCES

Table 8-1 lists those companies which produce benzene from petroleum in Canada, with an indication of the total capacities of the various plants in 1975 (4), and 1977 (5-8).

The giant petrochemical complex recently completed by Petrosar Ltd. (a consortium of Polysar Ltd., Union Carbide Ltd., DuPont of Canada Ltd., and the Canadian Development Corporation) came on-stream in late 1977 (6). Thus, the impact of benzene production from this facility will not be felt in the Canadian benzene market until 1978. Also, as indicated in the table, planned expansions by Shell Canada Ltd. and Texaco Canada Ltd. are not expected to come on-stream until 1978.

The total capacity available for benzene production in 1977, from the figures presented in Table 8-1 (except as mentioned above), is 439 Gg/annum. This figure is expected to rise to around 700 Gg/annum by the end of 1978. Most of the benzene production facilities in Ontario, are located in the Sarnia area. Facilities for some 220 Gg/annum of benzene production are available in Ontario accounting for about 50 % of total Canadian production capacity. By the end of 1978, these figures for Ontario should rise to 470 Gg/annum, or about 70 % of Canadian capacity.

Table 8-2 contains estimates of benzene supply and demand in Canada



TABLE 8-1

COMPANIES PRODUCING BENZENE FROM PETROLEUM
IN CANADA AND TOTAL PLANT CAPACITIES,
1975 AND 1977
 (All figures in Gg/annum)

<u>COMPANY</u>	<u>TOTAL CAPACITY</u>	
	<u>1975</u>	<u>1977</u>
Esso Chemical Canada, Sarnia, Ont.	100	70
Gulf Oil Canada, Montreal East, Que.	68	100 ¹
Petrofina Canada, Pte-Aux-Trembles, Que.	82	116 ¹
Petrosar, Corunna, Ont.		165 ²
Polysar, Sarnia, Ont.	68	60
Shell Canada, Corunna, Ont.	33	33 ³
Sun Chem (Sun Oil), Sarnia, Ont.	40	40
Texaco Canada, Port Credit, Ont.	20	20 ⁴

¹ Including hydrodealkylation of toluene.

² Came on-stream in late 1977; under construction in 1975.

³ Being expanded to 100 Gg/annum by 1978.

⁴ More feedstock available (to 40 Gg/annum) when new refinery at Nanticoke is on-stream.



TABLE 8-2

ESTIMATES OF BENZENE SUPPLY AND DEMAND 1974-76AND FORECASTS FOR 1977

(All figures in Gg/annum)

	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
Capacity	380	410	440	540
Production	325	250	373	457
Domestic Consumption	239	207	253	282
Imports ¹	3.3	0.02	0.03	nil
Exports	52	59	86	209
Inventory Change	+37	-16	+34	-34
Amount Shipped ²	90.3	97.7	254.4 ³	n/a

n/a Figures not available.

¹ Reported by Statistics Canada, Pub. No. 65-203, "Imports - Merchandise Trade", (CITC* 406-21), 1977.

² Reported by Statistics Canada, Pub. No. 45-205, "Petroleum Refineries", (SIC 3651), 1975.

³ Statistics Canada, Ref. 9.

* CITC - Canadian International Trade Classification.



for 1974-77.

An estimate has been incorporated into the capacity figure for 1977 of the amount of benzene produced by the new Petrosar Ltd. facilities which came on-stream in late 1977. Canadian production is currently around 85 % of capacity. The extra capacity is probably unavailable because of repair and maintenance operations. A significant drop in production occurred in 1975, likely due to a world-wide recession at that time.

The figures for amount of benzene shipped include exports, the remaining amount being domestic shipments. These figures, as reported by Statistics Canada, are misleading. In reporting shipments to Statistics Canada some refineries include benzene shipments for use as petrochemical feedstocks in their total petrochemical feedstock shipment figure. Thus these shipments are not included in Statistics Canada's shipment figures for benzene (9).

Any benzene which is used captively to produce other petrochemicals may not be included in shipment figures. Two companies that use benzene captively are Gulf Oil Canada Ltd., Montreal, Quebec (to manufacture cumene and cyclohexane) and Polysar Ltd., Sarnia, Ontario (to manufacture styrene).

The small amounts of benzene imported probably reflect local balance of trade or economic arrangements.

Separate figures for production of benzene in Ontario are not available, but a reasonable estimation may be made by reference to Table 8-1 and its subsequent discussion. Ontario presently has about 50 % of Canadian capacity, and thus accounts for 50 % of Canadian production.



The major exporters of benzene are believed to be Petrofina Canada Ltd., Point-Aux-Trembles, Quebec, SunChem Ltd., Sarnia, Ontario, and Esso Chemical Canada Ltd., Sarnia, Ontario (10). Petrofina exports mainly to overseas customers, and Esso Chemical to the Midland, Michigan plant of the Dow Chemical Company. The balance of benzene export is probably made up of surplus stocks of the other major producers.

8.3.2.3 BENZENE FROM COAL CARBONIZATION

The principal purpose of coal carbonization in Canada at the present time is to manufacture coke for the primary production of iron and steel. The four largest coke manufacturing plants, producing over 90 % of the total Canadian coke, are owned and operated by integrated steel companies which not only utilize the coke in blast furnaces but also use the associated coke oven gas in several operations throughout the steel complex.

Coke is the residue from the destructive distillation of bituminous coal. Air is excluded during the coking process and the necessary heat for distillation is supplied from external combustion. During the heating process the volatiles are driven off, and the hydrogen contained in the coal reacts with carbon and nitrogen to form other compounds which are volatilized. The various volatile products are collected and processed to reclaim chemicals, coke oven gas, and coal tars. The hot residue, which is carbon with some inorganic compounds present as ash, is water quenched and is known as coke.

Benzene is isolated from two by-products of coke manufacture - coal tar and light oil. It should be noted, however, that no in-plant refining



of these by-products is carried out in Canada at the present time because of the relatively small size of chemical recovery (11).

Table 8-3 lists the production of coke in Canada for 1974-77 and estimates of the amount produced in Ontario. An estimate of the amount of benzene present in the light oil fraction obtained from coke manufacture is also listed. Between 9 and 15 gallons of coal tar are produced per ton of coke manufactured, but as coal tar only contains about 0.2 % benzene (equivalent to about 0.45 Gg in total production for 1976), recovery from this source is uneconomical in Canada so these figures are not included in the figures for recoverable benzene.

All coke produced in Ontario is from imported coal, mainly from the West Virginia coalfields of the United States. Coking operations in Eastern and Western Canada, however, use mainly Canadian coal.

The figures for coke production in Ontario are estimates based on 80 % of Canadian coke manufacturing facilities being located in Ontario (11). These facilities are located at the three major steel plants in Ontario: Algoma Steel Co., Sault Ste. Marie; Steel Co. of Canada (Stelco), Hamilton; and Dominion Foundries and Steel Ltd., (Dofasco), Hamilton. All three of these plants sell the recovered light oils to petrochemical companies for further processing. It is not known whether the petrochemical companies separate benzene from this light oil.

The light oil recoverable benzene figures were arrived at as follows: 3-6 gallons of light oil are produced per ton of coke and approximately 70 % of light oil is benzene. An average figure of 4.5 gallon light



TABLE 8-3

AMOUNTS OF COKE AND BENZENE PRODUCED IN
CANADA AND ONTARIO, 1974-77 FROM
COAL CARBONIZATION

(All figures in Gg/annum)

<u>PRODUCTION</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
Coke				
- Canada ¹	5454.8	5288.9	5300.3	5735.4 ²
- Ontario	4290.5	4160.0	4169.0	4511.2
Recoverable Benzene				
- Ontario	59.4	57.6	57.7	62.4
- Canada	75.5	73.2	73.3	79.4

¹ Reported in Statistics Canada, Pub. No. 45-002, "Coal and Coke Statistics (ISSN 0380-6847)", December issues 1974-76.

² Estimate from (1) above based on July 1977 Statistics.



oil/ton of coke was used, equivalent to 13.84 kg benzene/Mg of coke (1.38 % yield of benzene).

The coal tar recovered from coke manufactured in Ontario is, except for part of the output of one producer, also sold to petrochemical companies. The exception is Dofasco Ltd. who use limited quantities of coal tar in a captive refractory brick-making operation (11). The coal tar sold to petrochemical companies is likely blended with petroleum tars to produce asphalts and impregnation tars.

8.3.2.4 BENZENE IN GASOLINE

Benzene is present in all gasolines. The level of benzene in gasoline depends on numerous factors including the source of crude oil, the geographic location of the source and the refiner, the grade of gasoline, the refinery operations, and the seasonal blends produced by each refinery.

An average benzene concentration of 1.24 liquid volume percent (lv %) was found in a survey of several different U.S. gasolines carried out in 1976 by the U.S. National Institute for Occupational Safety and Health (NIOSH) (12). This value was determined by weighting average of concentration in the three grades of gasoline (premium, regular and unleaded) from four commercial brand service stations. A series of gasoline samples obtained from U.S. Gulf Oil refineries in October 1976 showed an overall average of 1.25 lv % benzene in three grades of leaded gasoline (13). The highest value reported was 2.39 lv % and the lowest 0.54 lv %.



With the exception of alkylate and butane fractions from petroleum refining, essentially all products manufactured for blending into finished motor gasoline contain benzene in concentrations ranging from 0.5 to 8 lv % (3). Table 8-4 presents the benzene contents of gasoline blending components produced at two U.S. refineries (3). Data on the benzene content of these individual streams are limited and should be considered as rough estimates. Table 8-5 presents the aromatic content, including benzene, in some gasoline blending streams of an Ontario refinery (14).

It can be seen from these figures that the major sources of benzene in gasoline are the heavy reformat (light reformat is used for aromatics extraction) and catalytically cracked gasoline streams.

Gasoline produced in Ontario refineries is believed to contain about 1 lv % benzene (15), with gasoline produced Canada wide containing 1-5 lv %. The total amounts of motor gasoline shipped in Canada (16) were 34 G1 in 1974 and 35 G1 in 1975. Assuming a conservative figure for benzene content in motor gasoline of 1 lv %, the amounts of benzene present in motor gasoline shipped during 1974 and 1975 would be 337 M1 (296 Gg) and 351 M1 (308 Gg) for these years. It can be seen from these data that because of the large volumes consumed in Canada, the amount of benzene present in gasoline totals almost as much as the benzene produced for petrochemicals usage. It is estimated that about 110 Gg of benzene was present in gasoline used in Ontario during 1977, based on available data indicating sales of 12.7 GL of gasoline for road use (40).

The petroleum refineries use very little extracted benzene in their operations, (4.1 Gg in 1974 (16)). The vast majority of benzene present



oil/ton of coke was used, equivalent to 13.84 kg benzene/Mg of coke (1.38 % yield of benzene).

The coal tar recovered from coke manufactured in Ontario is, except for part of the output of one producer, also sold to petrochemical companies. The exception is Dofasco Ltd. who use limited quantities of coal tar in a captive refractory brick-making operation (11). The coal tar sold to petrochemical companies is likely blended with petroleum tars to produce asphalts and impregnation tars.

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TABLE 8-5

AROMATICS CONTENT OF REFINERY STREAMS USED FOR GASOLINE
BLENDING IN AN ONTARIO REFINERY (14)

	CRUDE DISTILLATION		REFORMER		NO. 1 FLUID CRACKING UNIT		NO. 2 FLUID CRACKING UNIT	
	Producing Gg/annum	% of Stream	Producing Gg/annum	% of Stream	Producing Gg/annum	% of Stream	Producing Gg/annum	% of Stream
Benzene	4.52	2.32	14.34	3.04	1.10	0.29	0.95	0.48
Toluene	0.43	0.22	70.89	15.03	11.14	2.94	7.51	3.81
Xylenes	--	--	93.48	19.82	26.14	6.90	15.85	8.03
Ethylbenzene	--	--	16.22	3.44	4.01	1.06	3.02	1.53
Cumene	--	--	0.71	0.15	0.53	0.14	0.25	0.13
Naphthalene	--	--	--	--	1.06	0.28	0.67	0.34



in gasoline occurs as a component of the various blended refinery streams. However, with restrictions on the use of leaded gasolines, the level of benzene in gasoline is expected to increase as more of the reformat fraction is used in gasoline blending to improve octane ratings.

8.3.3 USES OF BENZENE (EXTRACTED)

For many years the largest outlet for benzene was in blends with gasoline. Benzene was used with gasoline because of its high anti-knock value and its tendency to lessen starting difficulties. During World War II the use of benzene in the chemical industry expended rapidly. With the great rise in the demand and price of benzene for chemical manufacture during the post war years, the use of benzene in motor fuel blends has almost ceased in North America. At the present time chemical usage accounts for almost all of the benzene consumed in North America.

Figure 8-1 shows the products derived from benzene. The major products are seen to be ethylbenzene, cyclohexane, cumene, alkylbenzenes, maleic anhydride, chlorobenzene, and nitrobenzene. In the Canadian petrochemical industry, only ethyl benzene, styrene, cumene, cyclohexane, and maleic anhydride are manufactured as primary derivatives of benzene, with only ethylbenzene and styrene being manufactured in Ontario.

An estimate of the end-use pattern for benzene in Canada in 1977 is presented in Table 8-6. The manufacture of ethylbenzene to produce styrene is the major use of benzene. At the present time all ethylbenzene produced from benzene in Canada is manufactured in Ontario by two



FIGURE 8-1 USES OF BENZENE AND DERIVATIVES

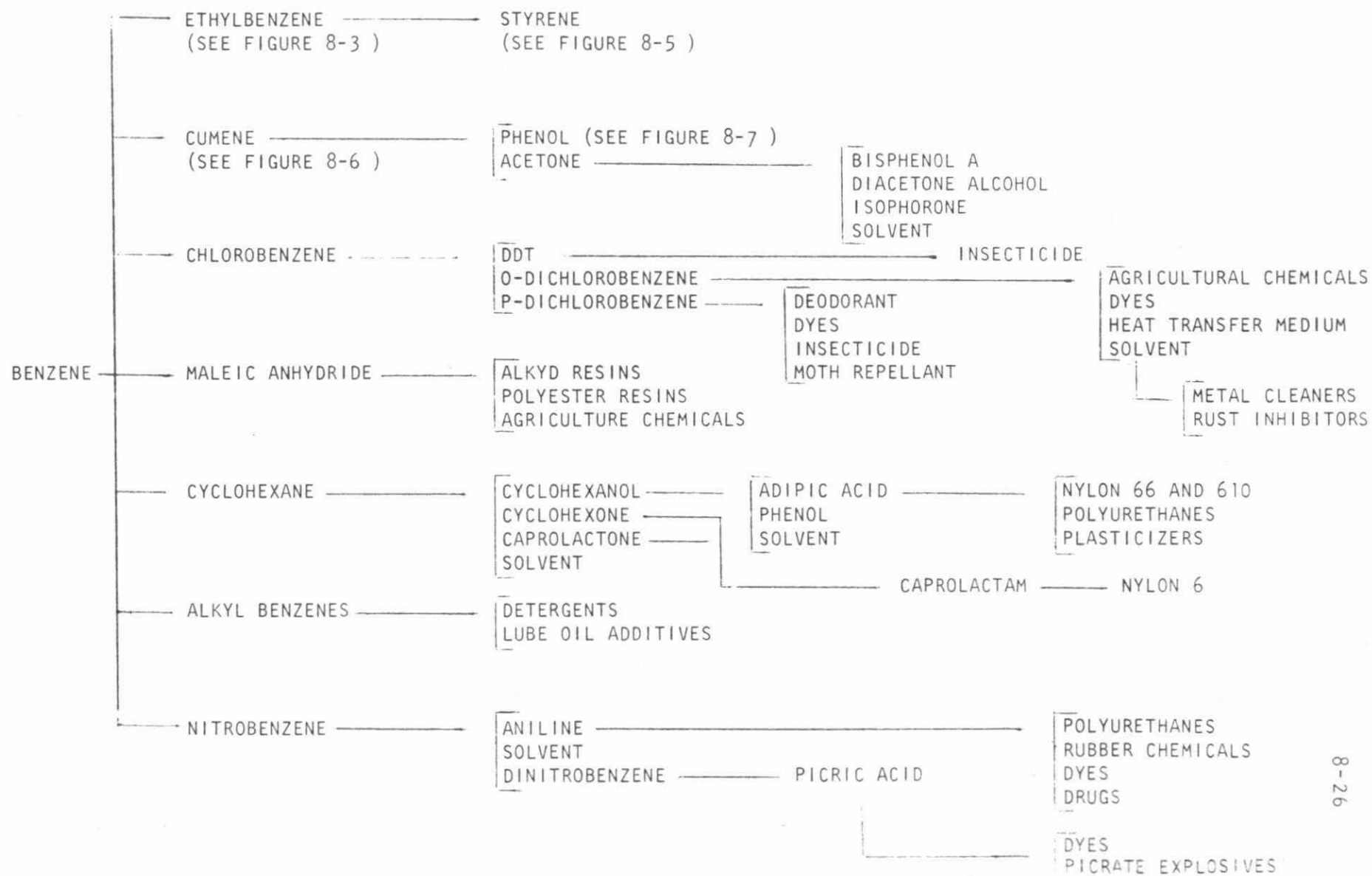


TABLE 8-6

ESTIMATED END-USE PATTERN FOR BENZENE
PRODUCED IN CANADA IN 1977

<u>USE</u>	<u>% OF PRODUCTION</u>
Ethylbenzene (Styrene)	28
Cumene	6
Cyclohexane	14
Maleic Anhydride	1
Miscellaneous	12
Exports	46
Inventory Change	-7
	<hr/>
	100



companies - Polysar Ltd. and Dow Chemical Co. of Canada, both located in Sarnia. The combined ethylbenzene production capacity of these two companies is about 200 Gg/annum. However, Dow Chemical of Canada may use some of its production facilities to produce glycols instead of ethylbenzene (17), so in some years total styrene production may be as low as 130 Gg/annum.

Cumene and cyclohexane are both manufactured by Gulf Oil Co. of Canada, Montreal East, Quebec. Maleic anhydride is manufactured by Monsanto Ltd. at La Salle, Quebec. Production of these chemicals account for about 90 Gg of benzene consumption per annum.

Table 8-7 presents a breakdown of uses by various industries as reported by Statistics Canada (16, 18-21). The only year for which figures are complete (1974) show a total consumption in these industries of 97 Gg of benzene. The benzene used by petroleum refineries is probably used as a gasoline blend, but this is not certain. The 0.89 Gg of benzene used by paint and varnish manufacturers is almost certainly used as a solvent.

The largest uses of benzene are the manufacturers of organic chemicals. However, as there are not more than three major producers for any of the high volume benzene derivatives produced in Canada, Statistics Canada does not release production figures for confidentiality reasons. Thus the 71 Gg of benzene consumed in this industrial category is probably used in the manufacture of detergents and surfactants, as a solvent or carrier, and in the manufacture of speciality chemicals



TABLE 8-7CONSUMPTION OF BENZENE BY INDUSTRY

(All figures in Gg/annum)

<u>INDUSTRY</u>	<u>SIC</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>REF.</u>
Petroleum Refineries	3651	n/r	4.09	n/r	16
Paint & Varnish Manufacturers	375	0.02	0.89	n/a	18
Manufacturers of Industrial Chemicals	3781-3	69.63	71.03	n/a	19
Miscellaneous Chemical Industries	3791-9	n/r	7.63	11.01	20
Manufacturers of Plastics and Synthetic Resins	373	5.14	13.32	n/a	21

n/a Figures not available.

n/r Figures not reported.

SIC Standard Industrial Classification



for the rubber and plastics industries.

The miscellaneous chemical industries category includes several hundred small companies producing a variety of different products. Benzene usage in this category is probably as a solvent in printing inks, or as a precursor or solvent for specialty chemicals in the production of disinfectants, pesticides, polishes, adhesives and cements. Benzene usage in the plastics and synthetic resins industry is likely as a solvent and carrier in polymerization processes.

8.3.4 MARKET FORECAST

Table 8-8 presents a forecast of benzene supply and demand in Canada to 1990, and average annual consumption growth rates.

Current expansions which are either just completed or nearing completion in Ontario (mainly at Sarnia locations) are estimated to fulfill Ontario (and most Canadian) requirements through 1980. The Petrosar facility just completed at Sarnia came on-stream in late 1977, and will be fully operational in 1978. When fully operational, this facility will consume 27 Ml/day of Canadian crude oil to produce 165 Gg/annum of benzene and 125 Gg/annum of toluene and xylene mixture, as well as 1.27 Ml/day of gasoline. The bulk of the petrochemical output will be sold to the three major shareholders - Polysar Ltd., DuPont of Canada Ltd., and Union Carbide Canada Ltd. Some production will be sold to Shell Canada Ltd.

The Shell aromatics facility at Sarnia, currently producing around 33 Gg/annum of benzene, is being expanded to produce 100 Gg/annum of



TABLE 8-8

FORECAST FOR BENZENE SUPPLY AND DEMAND IN
CANADA TO 1990

(All figures in Gg/annum)

	<u>1977</u>	<u>1980</u>	<u>1985</u>	<u>1990</u>
Capacity	540	750	885	965
Production	457	636	807	868
Domestic Consumption	282	422	625	777
Imports	nil	nil	nil	nil
Exports	209	214	182	91
Inventory Change	-34	nil	nil	nil

AVERAGE ANNUAL CONSUMPTION GROWTH RATES

1976 - 1980 = 14 %

1980 - 1985 = 8 %

1985 - 1990 = 4.5 %

1976 - 1990 = 8.5 %



benzene by 1978. Texaco Canada Ltd.'s new refinery at Nanticoke is expected to produce about 40 Gg/year of benzene when fully on-stream in 1978. However, this extra feedstock may not have a large effect on the benzene market as Texaco may have to close its Port Credit aromatics facility until a market is found for the extra benzene capacity (22).

Polysar Ltd. has recently completed a plant to produce 320 Gg/annum of ethylbenzene and 270 Gg/annum of styrene. Some of the feedstock for this plant will come from the Petrosar facility.

A major shift in benzene end-use patterns can be expected if a new cumene plant is built in Canada. If a long-term contract can be negotiated with a U.S. phenol producer, a cumene plant may be built in Sarnia (5).

The Alberta Energy Resources Conservation Board have recently awarded a contract to a consortium known as the Petalta group (Alberta Energy Co. Ltd., Mitsubishi Chemical Co., Mitsubishi Corp., and Hudson's Bay Oil and Gas Co. Ltd.) to produce benzene and other liquid by-products from natural gas condensates. The Petalta group plan to build a \$ 227 million plant in Saskatchewan that would produce 1.55 Ml/day (1.36 Gg/day) of benzene and 4.65 Ml/day of other liquid by-products from 7.5 Ml/day of pentanes-plus condensates (23). The project is expected to be completed by 1979-1980.

A long term possibility for benzene production is by manufacture from coal by liquifaction. Presently, technology is available to produce aromatics by coal liquifaction, but the process is still economically



unfeasible. However, with crude oil prices expected to rise and with domestic natural gas and oil supplies dwindling, this process could become of major significance in the next 10-15 years.



8.4 TOLUENE

8.4.1 INTRODUCTION

Toluene ($C_6H_5CH_3$) is the second member of the homologous series of aromatic compounds. It is a clear colorless, refractive non-corrosive liquid and has a distinctive "aromatic" odor similar to but milder than benzene. Its principal uses are as a gasoline blend, and as a chemical raw material in the synthesis of benzene and other compounds such as toluene diisocyanate (used in polyurethane manufacture), benzyl chloride, phenol and benzoic acid. It also has major use as a solvent.

Toluene is commercially produced in North America from petroleum and coal. It is a significant component of light oil recovered from coal carbonization (coking) operations. Toluene is also a minor component of coal tar recovered from these operations. Toluene is a minor component of crude petroleum, but is principally produced from petroleum by the hydroforming of selected petroleum naphthas which are rich in naphthenic hydrocarbons (24).

The first special emphasis on toluene as an important chemical occurred during World War I. At this time, trinitrotoluene (TNT) became the preferred high explosive and large quantities of toluene were required for the manufacture of this material. In order to satisfy this demand, toluene was obtained from petroleum sources for the first time to augment the supply from coal carbonization sources. Its production from petroleum was discontinued after World War I because the price was prohibitive for peace time use at that time.



About 1940 a process for converting petroleum naphthenes (cyclo-alkane compounds) to aromatics became commercialized. This process was developed primarily to make high quality gasolines. The entry of the U.S. to World War II in 1941, escalated the demand for toluene resulting in maximum production of 'toluene hydroformate' which was subsequently purified to give high-nitration-grade toluene for TNT manufacture. This development provided the basis for the huge petroleum aromatics industry which has resulted from the reforming-extraction processing of selected naphthas from crude oil. At the present time, toluene production from petroleum accounts for over 95 % of the amount of toluene produced in North America, the balance coming from by-product separation from coal carbonization operations.

8.4.2 PRODUCTION AND SOURCES

8.4.2.1 PRODUCTION FROM PETROLEUM AND NATURAL GAS

Toluene can be obtained from several petroleum or petrochemical processes, such as reforming, hydrocracking, steam cracking, and catalytic cracking. In Canada, the principal method of manufacture is, however, by separation from the reforming process.

In this process, naphthenes and paraffins in a naphtha fraction from crude oil are catalytically reformed to yield a high octane component (higher aromatic content) for gasoline blending. The toluene and other aromatic hydrocarbons are removed from the reformed product, or a special fraction of the product, by solvent extraction, and the extracted aromatic mixture is fractionally distilled to produce toluene as well as



benzene, xylenes and other aromatic hydrocarbons. The toluene fraction from this process can vary from 20-40 % of the final product, depending upon the choice of boiling range of the reformat fraction subjected to solvent extraction (25).

The cracking of paraffins (ie propane and n-butane) found in natural gas or heavier hydrocarbons (ie natural gas condensates, naphtha, and gas oil) for the manufacture of olefins (primarily ethylene and propylene) results in the formation of pyrolysis gasoline as a by-product. The quantity produced depends on the type of feed used and the conditions of cracking. Usually the amount of pyrolysis gasoline, which contains a high proportion of aromatics, is too small to make recovery of toluene from it economically attractive (26). However, heavier feeds can yield substantial volumes of pyrolysis gasoline, making aromatics separation economical. Aromatics, including toluene, are separated from pyrolysis gasoline by solvent extraction and fractional distillation, as for separation from reformates. Pyrolysis gasoline is often used as a supplementary feed to reformat extraction.

An additional source of toluene is as a by-product of the dehydrogenation of ethylbenzene to produce styrene. For each 50 Gg of styrene produced, 2.0 to 3.5 Gg of by-product toluene are obtained. With current Canadian styrene production estimated at 150 Gg/annum, the amount of by-product toluene produced may be 6.0 to 10.5 Gg/annum. All of this by-product toluene is normally recovered and either used or sold to other petrochemical producers.



Table 8-9 lists the Canadian producers of toluene, with estimates of production capacity for 1975 (4) and 1977 (5-8).

The Petrosar Ltd. facility at Corunna, Ontario is presently bringing its toluene and xylenes production on-stream (6). Thus, the impact of toluene production from this facility will not be felt in the Canadian market until mid-1978. The planned expansion by Shell Canada Ltd. will not be completed until mid-1978.

The total capacity for toluene production, from the figures presented in Table 8-9 (except for as mentioned above) is about 380 Gg/annum in 1977. This figure is expected to rise to about 510 Gg/annum by the end of 1978. The production capacity for toluene in Ontario for 1977 is about 200 Gg/annum which accounts for about 55 % of Canadian production capacity. By the end of 1978, these figures for Ontario should rise to around 340 Gg/annum, or almost 70 % of Canadian capacity.

8.4.2.2 TOLUENE FROM COAL CARBONIZATION

The principal purpose of coal carbonization in Canada at the present time is to manufacture coke for the primary production of iron and steel. The four largest coke manufacturing plants (producing over 90 % of all Canadian coke) are owned and operated by integrated steel companies who not only utilize the coke in blast furnaces, but also use the associated coke oven gas in several operations throughout the steel complex.

Coke is the residue from the destructive distillation of bituminous coal. Air is excluded during the coking process and the necessary heat for distillation is supplied from external combustion. During the



TABLE 8-9

CANADIAN PRODUCERS OF TOLUENE AND ESTIMATES
OF PRODUCTION CAPACITY FOR 1975 AND 1977

(All figures in Gg/annum)

<u>PRODUCER</u>	<u>TOTAL CAPACITY</u>	
	<u>1975</u>	<u>1977</u>
Esso Chemical Canada Ltd., Ioco, B.C.	35	30
Esso Chemical Canada Ltd., Sarnia, Ont.	39	39
Gulf Oil Canada Ltd., Montreal, Que.	40	52
Petrofina Canada Ltd., Pte-Aux-Trembles, Que.	n/a	84
Petrosar Ltd., Corunna, Ont.	-	127 ^{1,2}
Shell Canada, Corunna, Ont.	38	38 ³
Sun Chem (Sun Oil) Ltd., Sarnia, Ont.	127 ²	125
Texaco Canada, Mississauga, Ont.	16	16

n/a Not available.

¹ Coming on-stream in early 1978.

² Includes xylenes.

³ To be expanded to 45 Gg/annum by 1978.



heating process the volatiles are driven off, and the hydrogen present in the coal reacts with carbon and nitrogen to form other compounds which are volatilized. The various products are collected and processed to reclaim chemicals, coke-oven gas, and coal tars.

Toluene can be isolated from two by-products of coke manufacture—coal tar and light oil. It should be noted, however, that no in-plant refining of these by-products is carried out in Canada at the present time because of the relatively small size of chemical recovery (10).

Table 8-10 lists the production of coke in Canada for 1974-77 and estimates of the amount produced in Ontario. An estimate of the amount of toluene produced in the light oil fraction obtained from coke manufacture is also listed. Although 9 to 15 gallons of coal tar are produced per ton of coke manufactured, this coal tar contains less than 0.1 % toluene (equivalent to less than 0.2 Gg in total production of 1976) and hence recovery of toluene from coal tar is uneconomical in Canada. Figures are therefore not included for this source.

The figures for coke production in Ontario are estimates based on 80 % of Canadian coke manufacturing facilities being located in Ontario (10). These facilities are located at the three major steel plants in Ontario: Algoma Steel Co., Sault Ste. Marie; Steel Company of Canada Ltd., (Stelco), Hamilton; and Dominion Foundries and Steel Ltd. (Dofasco), Hamilton. All three of the plants sell the recovered light oils to petrochemical companies for further processing. It is believed that the petrochemical companies use this oil for gasoline blending. Some



TABLE 8-10

AMOUNTS OF COKE AND TOLUENE PRODUCED IN
CANADA AND ONTARIO 1974-77 FROM
COAL CARBONIZATION OPERATIONS

(Gg/annum)

<u>PRODUCTION</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u> ²
Coke				
- Canada ¹	5455	5290	5300	5735
- Ontario	4290	4160	4170	4510
Recoverable Toluene				
- Canada	15	15	15	16
- Ontario	12	11	11	12

¹ Reported in Statistics Canada, Pub. No. 45-002, "Coal and Coke Statistics (ISSN 0380-6847)", December Issues, 1974-76.

² Estimate from (1) above based on July 1977 Statistics.



benzene (the only component present in commercially significant concentration) may be separated.

The light oil recoverable toluene figures in Table 8-10 were calculated as follows: 3-6 gallons of light oil are produced per ton of coke and approximately 14 % of light oil is toluene. An average figure of 4.5 gallons of light oil/ton of coke was used, equivalent to 2.74 kg of toluene/Mg of coke (0.27 % yield of toluene).

8.4.2.3 TOLUENE IN GASOLINE

Toluene is present in crude oil in concentrations varying from 1.19 % to 1.39 % (25). As crude oil passes through the various stages of refining this toluene concentration is increased depending on the refinery stream or process used. In the final gasoline blend, the amount of toluene fluctuates from 2 to 10 % with the grade of gasoline produced (27, 41). The amount of toluene present in various gasoline blending streams of an Ontario refinery is presented in Table 8-5 (14).

These figures are from data obtained in the United States but it is believed that Canadian gasoline contains approximately the same amount of toluene. It is thus a major constituent of both motor and aviation gasoline. Recent figures for shipments of these two types of gasoline reported by Statistics Canada (16) are: motor gasoline, 34 G1 (1974) and 35 G1 (1975); aviation gasoline, 220 M1 (1974). Assuming a toluene concentration in gasoline of 6 %, the amount of toluene present in motor and aviation gasoline (using 1974 figures) would be 2,025 M1 (1756 Gg) for motor gasoline and 13 M1 (11 Gg) for aviation gasoline. The



amount of toluene present in gasoline far exceeds the amount separated for petrochemical use. Also, a large proportion of toluene that is separated for petrochemical use is blended back into gasoline to increase octane ratings.

8.4.3 USES OF TOLUENE

There are three principal uses of toluene. These are as an octane blend in gasoline, for the manufacture of benzene by hydrodealkylation, and as a solvent. Use as a chemical raw material accounts for only about 10 % of toluene usage in North America (28). Figure 8-2 presents a flow chart of the commercial uses of toluene and derivatives.

Historically, the largest use for toluene has been as an octane blend in gasoline. Prior to World War II, except during World War I when large quantities of toluene were required for explosives manufacture, essentially all toluene was used for this purpose. During World War II large volumes of toluene were again required for explosives manufacture. This coincided with the development of technology to produce aromatics in large volumes from petroleum. After World War II, the large demand for benzene to manufacture intermediates for the expanding detergent and plastics industries lead to the use of toluene to produce benzene by hydrodealkylation.

An estimate of the end-use pattern for toluene in 1976 is presented in Table 8-11.

Gasoline blending is the major use for toluene and it is likely that all Canadian producers use toluene for this purpose to some extent.





FIGURE 8-2 - USES OF TOLUENE AND DERIVATIVES IN NORTH AMERICA

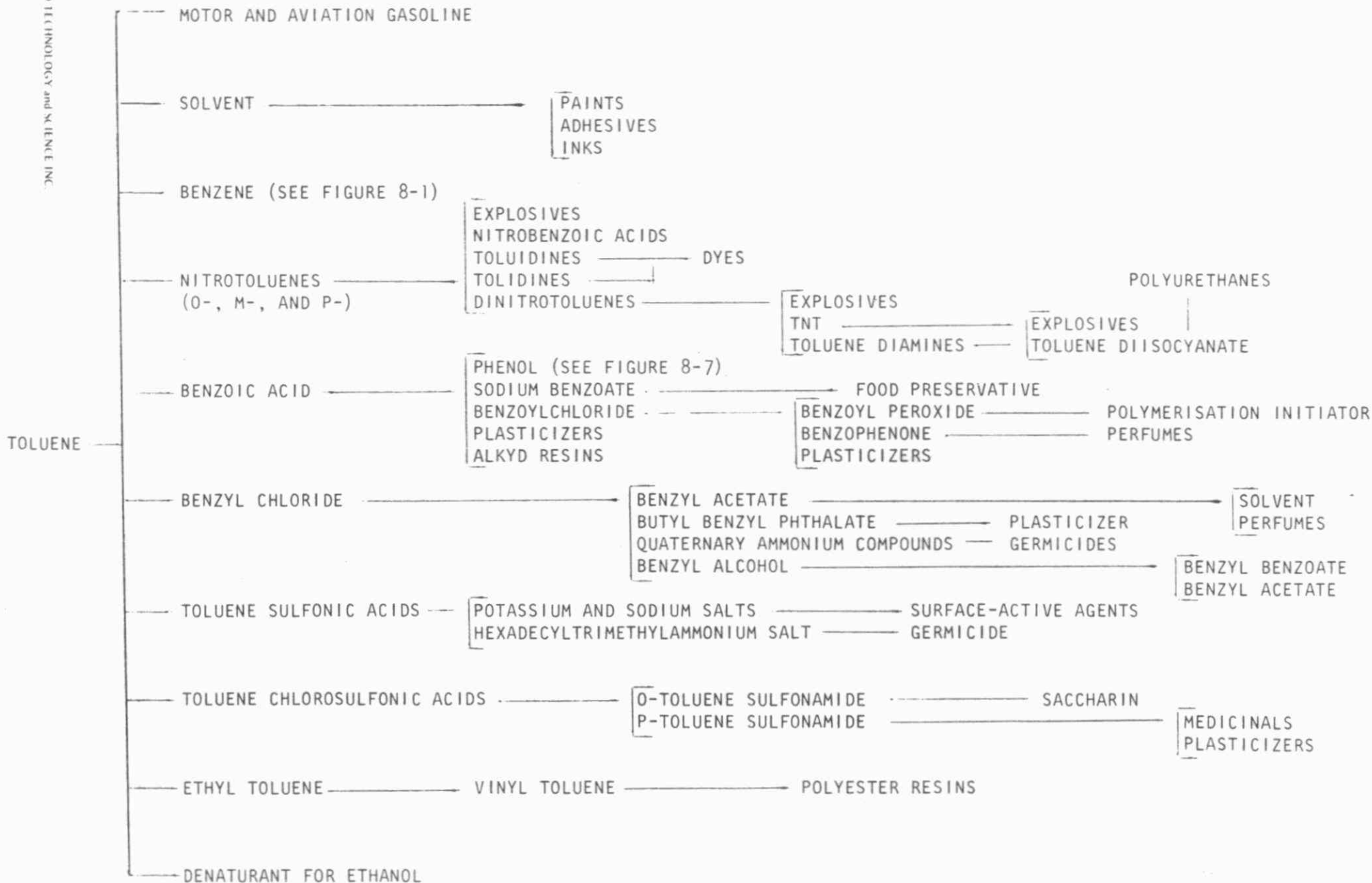


TABLE 8-11

ESTIMATED END-USE PATTERN FOR TOLUENE
PRODUCED IN CANADA IN 1976

<u>USE</u>	<u>% OF PRODUCTION</u>
Gasoline Blending	25
Benzene Production	20
Phenol Production	6
Solvent	10
Miscellaneous	5
Exports	34



The use of toluene to manufacture benzene by hydrodealkylation is the second largest use. However, the production of benzene from toluene by this process is more expensive than production of benzene by solvent extraction of petroleum reformates, so that the use of the hydrodealkylation process is strongly dependent on the relative prices of toluene and benzene.

Only two Canadian producers are known to have toluene hydrodealkylation facilities (both in Quebec). These are Gulf Oil Canada Ltd., Montreal, and Petrofina Canada Ltd., Pte-aux-Trembles. It is possible that other refiners have these facilities, but are not using them at present. Solvent usage accounts for a major part of the noncaptive use of toluene in Canada.

There is believed to be only one plant in Canada producing phenol from toluene. This is a plant operated by Dow Chemical Canada Ltd. in British Columbia which probably uses feed from the nearby refinery of Esso Chemical Ltd. at Ioco, B.C.

Miscellaneous uses of toluene are in the manufacture of explosives, surfactants and speciality chemicals for various industries.

The major exporter of toluene is Sun Chem Ltd., Sarnia, Ontario who ship most of their production to an affiliate in Toledo, Ohio. However, this is only a short term arrangement, and at present no market is available for this toluene when the export arrangement ends. This toluene will probably be returned to storage for use in gasoline blends until a market is found (5).



Table 8-12 summarizes the amounts of toluene used by various industries in Canada as reported by Statistics Canada for 1973-75. The amounts shipped and imported are also indicated. Available figures for 1976 are: Imports 7.9 Gg; amount used (9) 55.2 Gg; amounts shipped 52.5 Gg. The most complete figures (for 1974) show a total consumption in these industries of 54.4 Gg of toluene. Captive uses of toluene such as gasoline blending and hydrodealkylation to benzene are not included in these figures.

The use of toluene by paint and varnish manufacturers is as a solvent. Toluene is used interchangeably with xylene depending upon price fluctuations. However, toluene is the preferred solvent in this application because it is faster drying. Manufacturers of plastics and synthetic resins probably also use toluene as a solvent.

The use of toluene by miscellaneous chemical industries includes the use of toluene in explosives manufacturing. Two companies that share most of Canada's explosives business are Canadian Industries Limited (CIL) and DuPont of Canada Ltd. C.I.L. has an explosives plant at Nobel, Ontario, but it is not known whether trinitrotoluene manufacture from toluene is carried out at this facility. Other uses of toluene in this industrial category are probably solvent uses.

Manufacturers of industrial chemicals use toluene in the production of phenol and surfactants, with other uses being as a solvent and precursor for speciality chemicals used in pesticides, polishes, adhesives and cements. The use of toluene by the manufacturers of soaps and



TABLE 8-12

AMOUNTS OF TOLUENE USED BY CANADIAN INDUSTRIES
(1973-75) AND TOTAL AMOUNTS SHIPPED
AND IMPORTED
(All figures in Mg/annum)

	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>REF.</u>
Amounts Shipped	n/a	48,000	n/r	16
Amounts Imported	n/a	45,100	5,800	29
Amounts Used				
Paint & Varnish Manufacturers (SIC 375)	15,900	19,900	n/a	18
Manufacturers of Plastics & Synthetic Resins (SIC 373)	2,400	1,600	n/a	21
Miscellaneous Chemical Industries (SIC 379)	n/a	8,400	10,800	20
Manufacturers of Industrial Chemicals				19
A. Manu. of Pigments & Dry Colors (SIC 3781)	0.8	1.6	n/a	
B. Manu. of Industrial Chemicals (inorganic) (SIC 3782)	7.7	n/r	n/a	
C. Manu. of Industrial Chemicals (organic) (SIC 3783)	24,100	24,100	n/a	
Manufacturers of Soaps and Cleaning Compounds (SIC 376)	n/a	348	357	30

n/a = figures not available

n/r = figures not reported



cleaning compounds is most likely as a solvent in industrial cleaner formulations.

8.4.4 MARKET FORECAST

Current expansions which are either just completed or nearing completion in Ontario are estimated to fulfill Canadian (and Ontario) requirements for toluene through 1980. The Petrosar Ltd. facility just completed at Sarnia is expected to come on-stream in late 1977, and be in full operation by 1978. When fully operational, this facility will product 125 Gg/annum of toluene and xylene mixture. Shell Canada is also expanding its toluene extraction capacity by 20 % to be completed by 1978.

Most of the current expansions of toluene capacity are believed to be intended to supply toluene as a high octane blend for gasoline. The demand for toluene as a chemical raw material is not large in Canada at the present time, and most surplus toluene is either blended into gasoline, hydrodealkylated to benzene, or exported. Presently Sun Chem (Sun Oil) Ltd. of Sarnia export all of the toluene production from their new aromatics extraction facility to an affiliate in Toledo, Ohio. This arrangement is expected to end in 1979 and Sun Chem has to find a market for the toluene. They could build a hydrodealkylation unit to produce benzene from toluene, but there is currently no market for this extra benzene in the Sarnia area. The surplus toluene will most likely be returned to the unleaded gasoline pool in 1979, until a market can be found for it.



The toluene solvent market, which is the most important for domestic producers, cannot expand significantly. Toxic solvents in coatings, adhesives and other resinous formulations are under heavy criticism, effectively reducing the solvent market to prevent further expansion.

A toluene-oxidation plant to produce phenol will probably not be built in Ontario, as large scale cumene to phenol plants are more economical. However, Ontario could support a larger producer of toluene diisocyanate (TDI). The current producer, Allied Chemical Ltd., Corunna, imports toluene diamine for TDI manufacture.

Another possible market for toluene is an isocyanate facility proposed by Valley Chemicals of Cornwall. The facility was first proposed to produce both aniline and methylene-dipara-phenylene isocyanate (MDI), for manufacture of rigid urethane foams, in 1974. The project would need perhaps 40 Gg/annum of benzene feed, which could be obtained from dealkylation of surplus toluene.

Most toluene is used as an octane blend in gasoline. This use is expected to increase substantially as lead alkyl additives are phased out of the market. A possible controlling factor in this application is the use of methyl cyclopentadienyl manganese carbonate as an antiknock additive. This product, still in short supply, is used in about 50 % of the unleaded gasolines produced in the United States. Its octane cost is considerably higher than lead alkyls, but gasoline containing this product has not been restricted by the U.S. Environmental Protection Agency (31). As the use of this product becomes more wide-spread, its use in Ontario-produced gasoline could become a possibility.



8.5 XYLENES AND ETHYLBENZENE

8.5.1 INTRODUCTION

Xylenes and ethylbenzene are eight-carbon-atom aromatic hydrocarbons of the benzene family. The term 'xylenes' generally applies to a mixture of any two or three of the dimethylbenzene isomers, ie ortho-, para- and meta-xylenes. A frequently accepted nomenclature for the xylenes plus ethylbenzene is 'mixed xylenes'. Xylene is a colorless, flammable liquid with an aromatic odor similar to that of benzene and toluene. The principal uses of mixed xylenes are as octane blends in gasoline, as solvents, and for the production of individual isomers. For each of the four isomers there is one principal derivative which accounts for almost 100 % of the production. Ethylbenzene is used to make styrene, p-xylene to make terephthalic acid, o-xylene to make phthalic anhydride and m-xylene to make isophthalic acid.

Xylenes are commercially produced by two methods - coal carbonization and by petroleum refining methods. In the carbonization of coal, the light oil recovered from volatile distillation products contain a small proportion of xylenes. Petroleum feedstocks also contain a small proportion of xylenes, and catalytic reforming of these greatly increases the proportion of xylenes, which are recovered by solvent extraction and fractional distillation. Ethylbenzene is principally produced by synthesis from benzene and ethylene.

Prior to World War II, all xylenes were produced from coal derived sources. The wartime demands for toluene gave impetus to the petrochemical



industry for the rapid commercialization of the reforming process to product aromatics. Continued postwar expansion of the reforming process to provide high-octane gasoline components has made a reservoir of C_6-C_{10} aromatics potentially available for petrochemicals. Xylenes constitute about 40 % of this reservoir. At the present time, production of xylenes from petroleum sources accounts for 99 % of the total xylenes production in North America (32).

8.5.2 PRODUCTION AND SOURCES

8.5.2.1 PRODUCTION FROM PETROLEUM

Approximately 96 % of the recovered xylene from petroleum sources is solvent extracted from reformate and the remaining 4 % is solvent extracted from pyrolysis gasoline.

In the reforming-separation processes, a petroleum naphtha fraction is catalytically reformed to produce a more desirable product (higher octane number) for use in gasoline blending. The xylenes and other aromatic hydrocarbons are removed from the reformed product by solvent extraction, and the extracted aromatic mixture is fractionally distilled to yield xylenes and other aromatic hydrocarbons, chiefly benzene and toluene. The yield of xylenes from these processes is usually 25-40 %. An average composition of the xylene mixture obtained from these processes is presented in Table 8-13 (32).

Pyrolysis gasoline is a by-product of the cracking of paraffins or heavier hydrocarbons to produce olefins. Pyrolysis gasoline contains a high percentage of aromatic compounds. Xylenes are extracted from



TABLE 8-13

AVERAGE COMPOSITION OF MIXED XYLENES FROM
EXTRACTED REFORMATE

<u>COMPOUND</u>	<u>%</u>
Toluene	2.9
Ethylbenzene	23.7
p-Xylene	16.7
m-Xylene	35.7
o-Xylene	20.5
C ₉₊ Aromatics	0.6
	<hr/>
	100.0



this refinery product by solvent extraction and fractional distillation.

Although ethylbenzene is a major component of mixed xylenes, the vast majority of ethylbenzene produced is synthesized from benzene and ethylene.

Table 8-14 lists those companies that produce xylenes from petroleum in Canada, with an indication of the total capacities of the various plants as of May, 1975 (4) and November, 1977 (5-8).

The large increase in xylene production capacity from 1975 to 1977 is most likely as a result of the substitution of lead alkyl additives in gasoline by xylenes to increase the octane rating. Not included in this table are xylene production figures for Petrosar Ltd. as these are reported as a toluene and xylene mixture (125 Gg/annum).

These figures indicate that total xylene capacity in Canada is almost 550 Gg/annum with capacity for about 250 Gg/annum being located in Ontario accounting for about 45 % of Canadian capacity.

At the present time, the only separated xylene isomers produced in Canada are o-xylene and ethylbenzene. Petrofina Canada Ltd., Pte-aux-Trembles, Quebec, separate about 12 Gg/annum of o-xylene which is shipped to BASF Ltd. in Cornwall, Ontario, for conversion to phthalic anhydride.

There is no separation of ethylbenzene from mixed xylenes in Canada at the present time. All ethylbenzene produced is synthesized from benzene and ethylene. There are currently two producers of ethylbenzene, both located in Sarnia, Ontario and these producers are Polysar Ltd. and Dow Chemical of Canada Ltd. with a combined styrene production capacity



TABLE 8-14

COMPANIES PRODUCING XYLENES FROM PETROLEUM
IN CANADA AND TOTAL PLANT CAPACITIES,
1975 AND 1977

(All figures in Gg/annum)

<u>COMPANY</u>	<u>TOTAL CAPACITY</u>	
	<u>1975</u>	<u>1977</u>
Esso Chemical Canada Ltd., Sarnia, Ont.	19	20
Gulf Oil Canada Ltd., Montreal, Que.	20	135
Petrofina Canada Ltd., Pte-Aux-Trembles, Que.	25	145
Shell Canada Ltd., Sarnia, Ont.	23	n/r
Sun Chem (Sun Oil) Ltd., Sarnia, Ont.	n/a	86
Texaco Canada Ltd., Mississauga, Ont.	16	55

n/a Figures not available.

n/r Figures not reported.



of about 200 Gg/annum (equivalent to about 210 Gg/annum of ethyl benzene capacity).

8.5.2.2 XYLENES FROM COAL CARBONIZATION

Coal carbonization in Canada is principally carried out to manufacture coke for the primary production of iron and steel. Two by-products of coking operations, light oil and coal tar, are sources of aromatic compounds. Xylenes are present in both fractions, but their percentage in coal tar is negligible (less than 0.1 %). However, xylenes constitute about 3 % of the light oil produced. It should be noted, however, that no in-plant refining of this light oil is carried out in Canada at the present time because of the relatively small size of chemical recovery (11).

Coke production in Ontario for 1976 is estimated to be 4170 Gg. This figure is estimated from the fact that 80 % of Canadian coke production capacity is located in Ontario. Canadian coke production for 1976 was 5300 Gg (33). Facilities for coke production in Ontario are located at three major steel plants; Algoma Steel Co. Ltd., Sault Ste. Marie, Steel Co. of Canada Ltd. (Stelco), Hamilton and Dominion Foundries and Steel Ltd. (Dofasco), Hamilton. All three of these plants sell their recovered light oils to petrochemical companies who use it either as a supplementary feed for aromatics production or as a gasoline blend.

The amount of recoverable xylenes from this light oil in Ontario would be about 2 Gg based on 1976 figures. This figure is calculated assuming 4.5 gallons of light oil produced per ton of coke, 3 % xylenes, and an average density of mixed xylenes of 0.727 g/cm^3 (34). This is equivalent



to a yield of 0.49 kg mixed xylenes per metric ton (1000 kg) of coke.

8.5.2.3 XYLENES IN GASOLINE

Xylenes are a major constituent of gasoline. They are present in varying quantities in many of the various petroleum fractions used to produce gasoline blends. The amount of xylenes present in gasoline blending streams of an Ontario refinery are presented in Table 8-5 (14). Most of the xylenes produced in Canada are blended into gasoline to improve octane ratings. No figures are available for the amount of xylenes present in finished gasoline, but the amount is estimated to be at least as high as the concentration of toluene (6 %).

8.5.3 USES OF XYLENES

Most of the xylenes produced in Canada are recycled to the motor gasoline pools of the producing refineries, or are exported as mixed xylenes. No figures are available for the amount of xylene used for these purposes, but an estimate based on production unaccounted for after adding up available figures for other uses indicates that about 90 % of production is either blended into gasoline or exported. A flow chart for commercial uses of xylenes and derivatives in North America is shown in Figure 8-3. A similar chart for phthalic anhydride, a principal xylene derivative, is shown in Figure 8-4.

The amounts of mixed xylenes used by various industries as reported by Statistics Canada are listed in Table 8-15. Amounts of xylenes imported and shipped are also included in the table.





FIGURE 8-3 USES OF XYLENES AND XYLENE DERIVATIVES

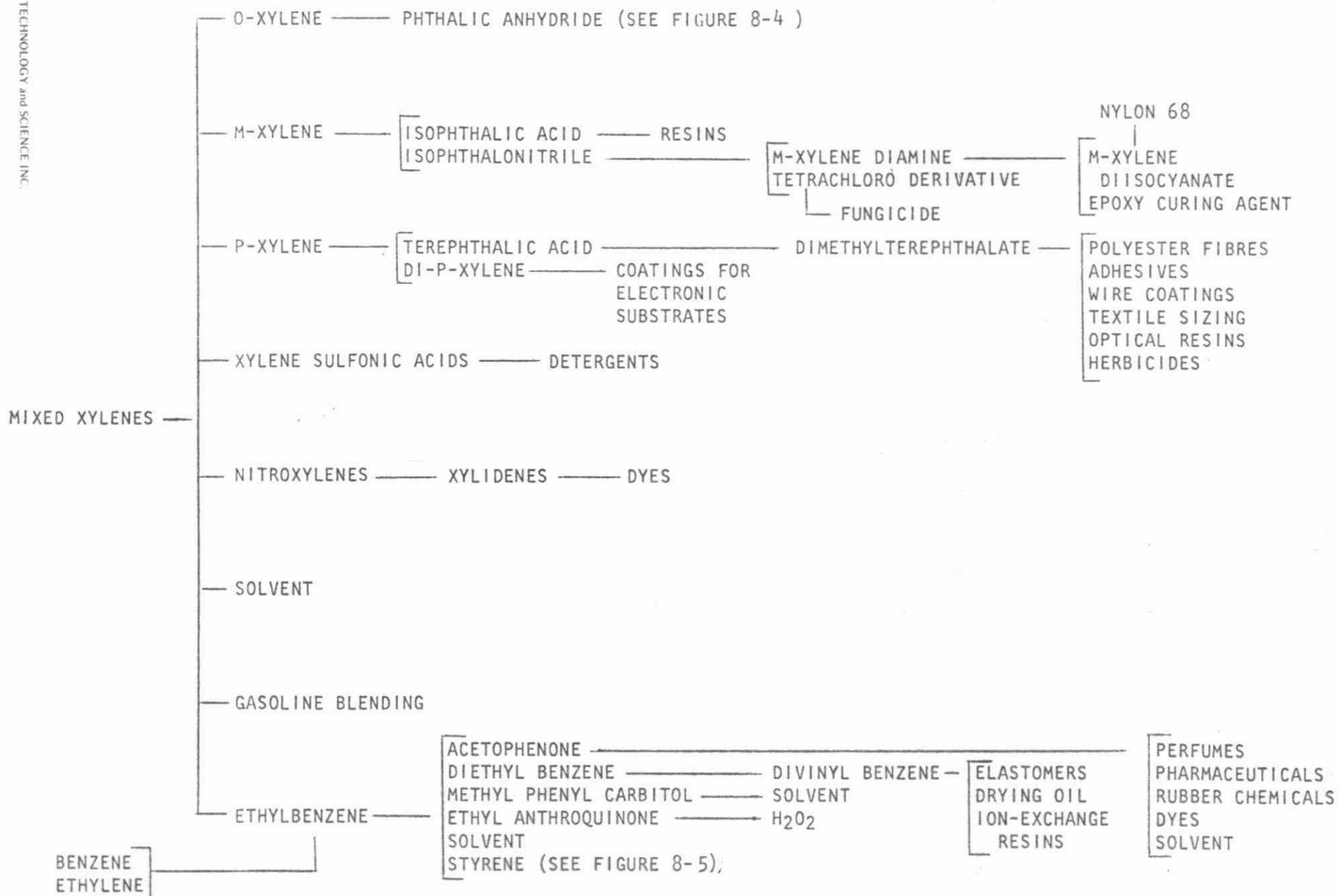


FIGURE 8-4 USES OF PHTHALIC ANHYDRIDE AND DERIVATIVES

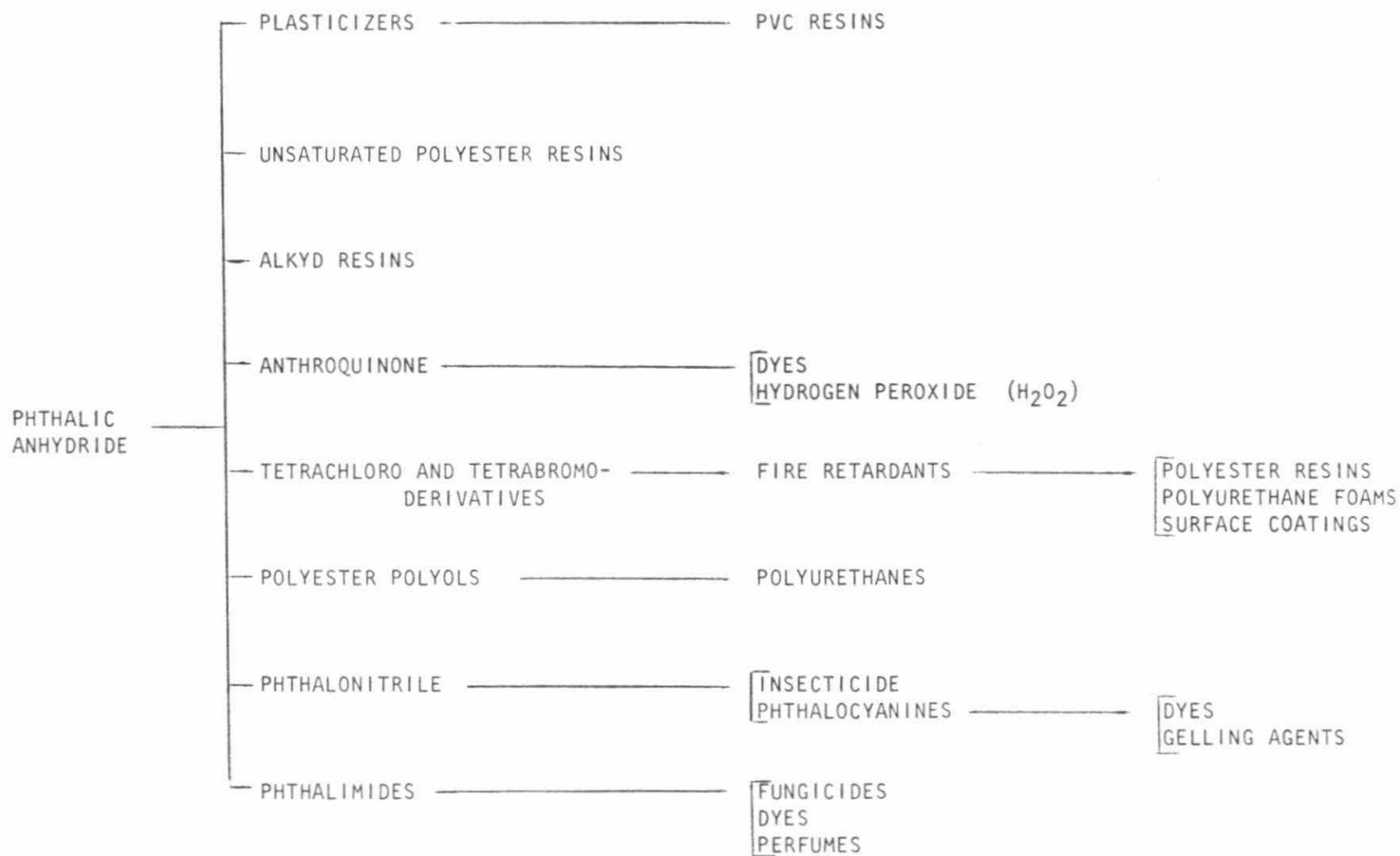


TABLE 8-15

AMOUNTS OF XYLENES SHIPPED, IMPORTED AND

CONSUMED BY INDUSTRY

(All figures in Mg/annum)

	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>REF.</u>
Amount Shipped	n/a	41,100	n/a	51,700	16
Amounts Imported	n/r	13,100	1,600	20,000	29
Amounts Consumed					
Manufacturers of Industrial Chemicals					19
A. Manufacturers of Pigments & Dry Colors (SIC 3781) ¹	136	4	n/a	n/a	
B. Manufacturers of Industrial Chemicals (organic) (SIC 3783)	43	124	n/a	n/a	
Miscellaneous Chemical Industries (SIC 379)	n/a	8,764	28,950	n/a	20
Paint & Varnish Manufacturers	22,034	22,532	n/a	n/a	18
Manufacturers of Plastics & Synthetic Resins (SIC 373)	13,387	4,042	n/a	n/a	21

¹ SIC Standard Industrial Classification
n/a Figures not available
n/r Figures not reported



Except for the category of miscellaneous chemical industries, the amounts of xylene listed in Table 8-15 are most probably used in solvent applications.

The amounts of xylene used in the miscellaneous chemical industries category include the amount of xylene used by the B.A.S.F. Ltd. plant at Cornwall, Ontario. This facility produces phthalic anhydride from o-xylene, the only known use of a xylene isomer (except ethyl benzene) as a chemical raw material in Ontario.

Ethylbenzene used as a chemical raw material in Ontario is synthesized from benzene and ethylene. There are currently two producers in Ontario; Dow Chemical of Canada Ltd. and Polysar Ltd. both located in Sarnia with combined production facilities of about 200 Gg/annum. It is believed that there is no separation of ethylbenzene from mixed xylenes carried out in Ontario or Canada at the present time.

8.5.4 MARKET FORECAST

There is presently only one petrochemical company in Canada which separates xylenes. This is Petrofina Canada Ltd. of Pte-aux-Trembles, Quebec who separate ortho-xylene. This company plans to build a new plant to produce about 65 Gg/annum of ortho-xylene. This plant will replace the existing 15 Gg/annum facility. Most of the ortho-xylene will be shipped to the B.A.S.F. Ltd. facility at Cornwall, Ontario for the manufacture of phthalic anhydride, and some will be exported (about 20 Gg/annum). The new facility is expected to be completed and on-stream by early 1979 (35).



Sun Chem (Sun Oil) Ltd., of Sarnia, Ontario plan to strip ortho-xylene from the xylene mixture produced at their new aromatics facility. Part of this feed will also be shipped to B.A.S.F. Ltd. at Cornwall. There is a possibility that Monsanto Ltd. or Reichhold Chemicals Ltd., who are both large producers of phthalic anhydride in the U.S., will build phthalic anhydride production facilities in Canada, providing a Canadian market for the rest of the ortho-xylene produced by Sun Chem Ltd., and Petrofina Canada Ltd.

The outlook for production of other xylene isomers in Canada is not good at the present time. The principal use of para-xylene is to manufacture terephthalic acid (TPA) and dimethyl terephthalate (DMT), used in the production of polyester fibres. The main producer of polyester fibres in Canada is DuPont Ltd., who have recently completed a new plant in Coteau-du-Lac, Quebec. However, the polyester fibre market is not good at the present time, so DuPont will probably not produce TPA or DMT until this market improves.

If the polyester market does improve significantly in the next few years, both Sun Chem Ltd. and Petrofina Canada Ltd. could separate para-xylene from their mixed xylenes streams after stripping ortho-xylene.

A consequence of this would be that Petrofina Ltd. could also recover ethylbenzene from their xylene stream. Petrofina has captive benzene available (currently mostly exported) and access to ethylene from Gulf Oil Canada Ltd.'s new plant at Varennes, Quebec. Petrofina Ltd. could become a producer of styrene using ethylbenzene feed from xylene isomer



separation and from synthesis with benzene and ethylene.



8.6.2.3 STYRENE IN GASOLINE

The concentration of styrene in motor gasoline is not known. However, taking a reasonable estimate of 0.5 % would correspond to about 160 Gg/annum based on the 1975 figure for gasoline shipments of 35 G1 (16).

It should be noted that none of the styrene produced from ethylbenzene is blended into gasoline. The styrene present in gasoline is either present in the original crude oil or is formed during one of the refining operations of gasoline production. About 60 Gg of styrene was used in gasoline in Ontario in 1977 based on a 0.5 % concentration of styrene in gasoline.

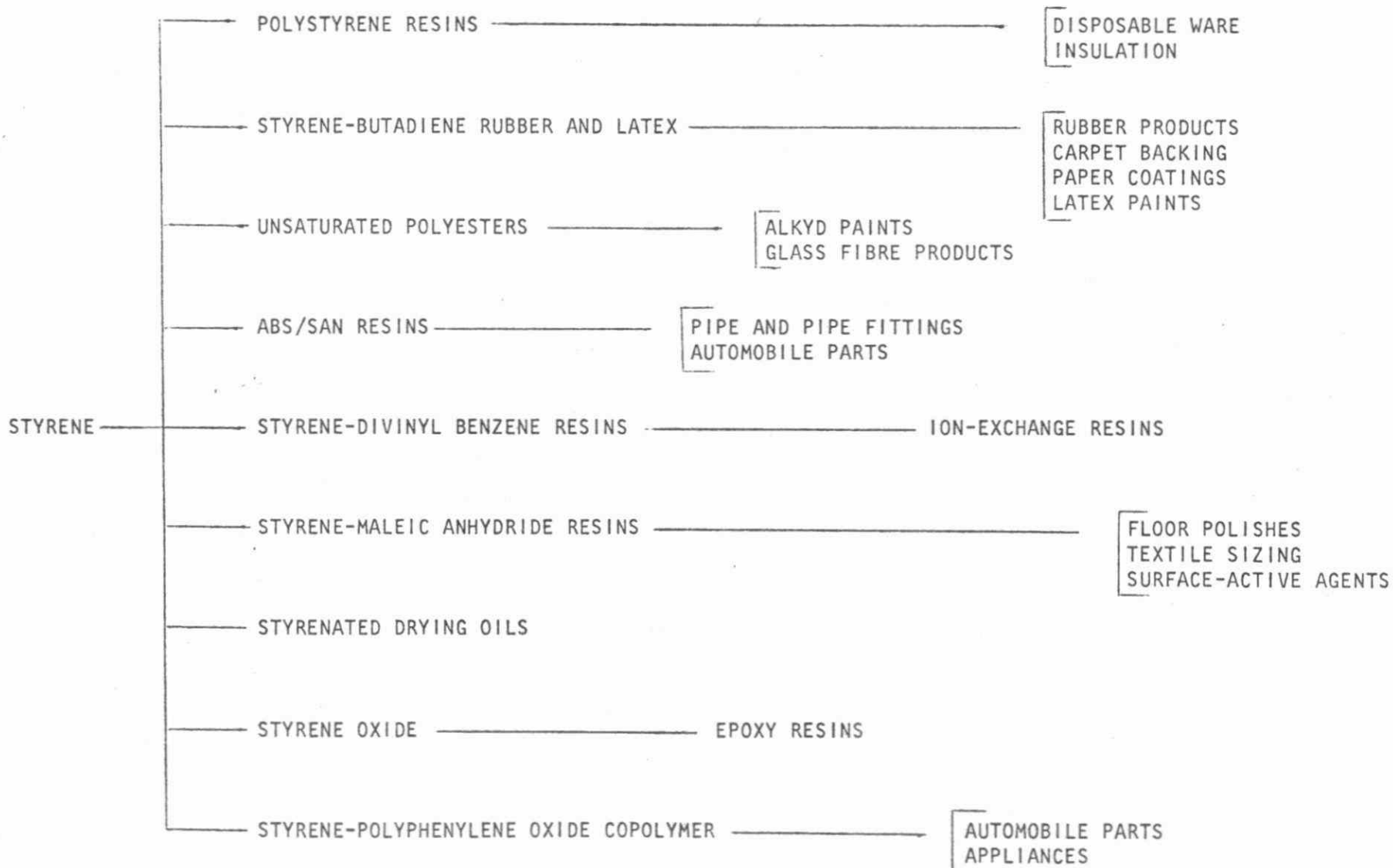
8.6.3 USES OF STYRENE

Almost all styrene that is commercially produced from ethylbenzene in Ontario is used as a monomer to manufacture a wide variety of homo and copolymers. Figure 8-5 is a flow chart of the uses of styrene and derivatives. A very small amount of styrene is used in solvent applications, usually as a solvent for styrenic polymers (15).

Table 8-16 presents the estimated end use pattern for styrene in Canada. It can be seen that the major use of styrene is in the manufacture of polystyrene, mainly as polystyrene foams.

Tables 8-17 to 8-20 present market breakdowns for the major products using styrene. It can be seen from these figures that the major uses of styrenic polymers are in the construction industry and the automotive industry. Total consumption of styrenic polymers in Canada for 1976 was about 320 Gg (including 20 Gg of unsaturated polyester consumption) with about 75 Gg being imported. Thus about 245 Gg of styrenic polymers were produced in Canada in 1976.



FIGURE 8-5 USES OF STYRENE AND DERIVATIVES

8.6 STYRENE

8.6.1 INTRODUCTION

Styrene ($C_6H_5CH=CH_2$) is the common name for the simplest and most important member of a series of unsaturated aromatic monomers. It is a clear, colorless, refractive liquid with a characteristic odor. Styrene is used extensively for the manufacture of plastics, including polystyrene, rubber-modified impact polystyrene, acrylonitrile-butadiene-styrene terpolymer (ABS), styrene-acrylonitrile co-polymer (SAN) and for the production of styrene-butadiene synthetic rubber (SBR).

Commercial manufacture of styrene began on a small scale around 1930 when the Dow Chemical Co. entered this field and ultimately became the first company in the United States to produce commercial styrene successfully. With the advent of World War II and the resulting loss of natural rubber resources, the production of styrene by Dow Chemical and a number of other U.S. chemical companies became of great importance. The styrene was polymerized with butadiene to produce synthetic rubber.

The huge expansion of styrene monomer production facilities laid the foundation for the postwar development of polystyrene and styrene copolymer plastics. Latices for paints and paper coatings, styrenated drying oils, styrenated alkyds as a base for many protective coatings, and styrene-polyester resins for laminated structures illustrate some further uses of styrene (36).

Canadian production of styrene began around 1943, when Dow Chemical and Polysar (then the Polymer Corporation of Canada) built facilities in the Sarnia area to produce styrene and SBR for synthetic rubber products



manufacturing.

Styrene has become basic to many sectors of the Canadian economy, ranging from synthetic rubber automobile tires to high impact polystyrene appliance parts and styrene-based latex paints.

8.6.2 PRODUCTION AND SOURCES

8.6.2.1 PRODUCTION FROM ETHYLBENZENE

At the present time, all styrene manufactured commercially in Canada is made by dehydrogenation of ethylbenzene. There are two producers of styrene monomer in Canada; Dow Chemical of Canada Ltd. and Polysar Ltd. both located in Sarnia, Ontario. Dow has capacity for about 85 Gg/annum of styrene production. Polysar has capacity for about 115 Gg/annum of production, and has recently completed a plant to produce a further 270 Gg/annum (10).

Dow Chemical of Canada Ltd. also uses some of its plant capacity to produce glycols, so that in some years their styrene production may be significantly lower than listed capacity (17).

8.6.2.2 STYRENE FROM COAL CARBONIZATION

Styrene is also found in gasoline and in light oil recovered from coal carbonization (coking) operations. The light oil recovered contains around 1 % styrene, and so about 1 Gg/annum of styrene is recoverable from this source based on 1976 coke production of 5300 Gg/annum (light oil recovered is about 2 % of coke production).



TABLE 8-16
ESTIMATED END-USE PATTERN FOR STYRENE
IN CANADA (1977)

<u>USE</u>	<u>% OF CONSUMPTION</u>
Polystyrene	55
Styrene-butadiene (SB) Rubber	16
SB Latex	11
ABS/SAN Resins	12
Unsaturated Polyesters	4
Miscellaneous	2
	<hr/>
	100



TABLE 8-17POLYSTYRENE MARKET BREAKDOWN

<u>END USE</u>	<u>PERCENT OF TOTAL CONSUMPTION¹</u>
Disposable Service Ware ²	32
Building and Construction ³	30
Packaging	22
Home and Commercial Furnishing	6
Leisure	5
Other	5
	<hr/>
	100

¹ Consumption currently 95 Gg/annum, with 15 Gg being imported (1976).

² Largest item is disposable drinking cups (foam).

³ Major use is as insulation (foam).



TABLE 8-18STYRENE-BUTADIENE RUBBER MARKET BREAKDOWN

<u>END USE</u>	<u>PERCENT OF TOTAL CONSUMPTION¹</u>
Tire Manufacture	80
Footwear	5
Wire and Cable Insulation	2
Miscellaneous	13
	<hr/> 100

¹ Consumption currently about 102 Gg/annum, with about 35 Gg being imported (1976).



TABLE 8-19

STYRENE-BUTADIENE LATEX MARKET BREAKDOWN

<u>END USE</u>	<u>PERCENT OF TOTAL CONSUMPTION</u> ¹
Carpet Backing	
- Primary and Secondary	50
- Foam	30
Paper Coatings	13
Tire Cord	4
Miscellaneous	3
	<hr/>
	100

¹ Consumption currently about 45 Gg/annum, with about 15 Gg being imported (1976).



TABLE 8-20

ACRYLONITRILE-BUTADIENE-STYRENE
TERPOLYMER/STYRENE-ACRYLONITRILE COPOLYMER
(ABS/SAN) MARKET BREAKDOWN

<u>END USE</u>	<u>PERCENT OF TOTAL CONSUMPTION¹</u>
Building and Construction ²	62
Transportation ³	16
Home and Commercial Furnishings	8
Leisure	4
Communications and Electronics	4
Other	6
	<hr/>
	100

¹ Consumption currently about 40 Gg/annum, with about 10 Gg being imported (1976).

² Essentially all use in manufacture of pipe and pipe fittings.

³ Largely automotive, eg Grills.



Table 8-21 lists the Canadian producers of styrene derivatives. Most of these producers are located in Ontario and include Dow Chemical Ltd. and Polysar Ltd., the Canadian manufacturers of styrene monomer.

The large number of manufacturers of unsaturated polyester resins illustrate the versatility of this as yet low volume usage of styrene derivatives. They are used mainly in the surface coating industry, and in the fibreglass industry. The latter industry uses glass-reinforced fibre in the manufacture of all kinds of molded parts. Pressure vessels, piping systems, tanks and automotive parts are just a few applications. However, the use of styrene in fibreglass products is very important from a population exposure point of view. Fibreglass products are used by the general population in such applications as car body repair, construction of boat hulls, etc. The formulations contain styrene both as a solvent and as a monomer. Upon mixing with the supplied catalyst, the styrene polymerizes with other ingredients in the product to form a hard, tough durable material. Any styrene not polymerized evaporates to the atmosphere. Thus any person working with these products in a confined space is subjected to an unusually high concentration of styrene vapors.

Table 8-22 lists the amounts of styrene used in various industries as reported by Statistics Canada. Total amounts of styrene consumed are also listed. Only part of the amount of styrene used by the primary producers, Dow Chemical and Polysar, is included in the industrial usage figures. These companies used about 100 Gg of styrene in 1975 to produce polystyrene and SB polymers. The remaining 30 Gg was used by the other producers of



TABLE 8-21

CANADIAN PRODUCERS OF STYRENE DERIVATIVES

<u>DERIVATIVE</u>	<u>PRODUCING COMPANY</u>	<u>PLANT LOCATION</u>
Polystyrene	B.A.S.F. Canada Ltd.	Montreal, Quebec
	Dow Chemical of Canada Ltd.	Sarnia, Ontario
	Monsanto Ltd.	Montreal, Quebec
	Polysar Ltd.	Cambridge, Ontario
	Potton Ltd.	Masonville, Quebec
S.B. Rubber	Polysar Ltd.	Sarnia, Ontario
S.B. Latex	Dow Chemical of Canada Ltd.	Montreal, Quebec
	Polysar Ltd.	Sarnia, Ontario
ABS/SAN Resins	Borg-Warner Ltd.	Cobourg, Ontario
	Monsanto Ltd.	Sarnia, Ontario
Unsaturated Polyester Resins	Alma Paint Ltd.	London, Ontario
	Ashland Chemicals Ltd.	Toronto, Ontario
	Bapco Paint Ltd.	Surrey, B.C.
	B.A.S.F. Canada Ltd.	Cornwall, Ontario
	Canadian General Electric Ltd.	Toronto, Ontario
	Canadian Occidental Ltd.	Fort Erie, Ontario
	Canadian Pittsburg Ltd.	Long Branch, Ontario
	Fiberglas Ltd.	Guelph, Ontario
	Fiberplast Ltd.	Winfield, B.C.
	Glidden Paints Ltd.	Toronto, Ontario
	MIA Chemical Ltd.	Toronto, Ontario
	Reichhold Chemicals Ltd.	Ste. Therese, Quebec
		Weston, Ontario
		Port Moody
	Schenectady Ltd.	Toronto, Ontario



TABLE 8-22

AMOUNTS OF STYRENE USED BY VARIOUS INDUSTRIES
AND TOTAL AMOUNTS OF STYRENE CONSUMED 1973-1976

(All figures in Gg/annum)

	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>REF.</u>
Amount Consumed	n/a	160	130	155	
Paint & Varnish Manufacturers (SIC 375)	2.5	1.2	n/a	n/a	18
Manufacturers of Plastics and Synthetic Resins (SIC 373)	43.2	46.0	n/a	n/a	21
Manufacturers of Industrial Chemicals (SIC 3783)	2.2	1.1	n/a	n/a	19
Total Used	47.9	48.3	50.2 ¹	n/a	

n/a Figures not available.

SIC Standard Industrial Classification

¹ Ref. 9.



styrene derivatives listed in Table 8-22.

8.6.4 MARKET FORECAST

Styrene will probably become a 500 Gg/annum commodity by 1980. The current capacity of about 200 Gg/annum will rise to 470 Gg/annum when the new styrene facility (270 Gg/annum) recently completed by Polysar Ltd. at Sarnia, Ontario comes into full production. Most of the feed for this plant will come from the new Petrosar refinery at Corunna, Ontario. However, Polysar plans to close down their older plant, currently 115 Gg/annum of styrene production capacity, until the extra styrene production is required (10).

A styrene facility is planned for Alberta to come into production by 1980. This facility is a project of Alberta Gas Ethylene Ltd. (AGE), Mitsubishi Chemical Co. of Japan, and Hudson's Bay Oil and Gas Ltd. (HBOG). The facility will combine ethylene produced by AGE with benzene extracted by HBOG from natural gas condensates. Styrene technology will be supplied by Mitsubishi Chemical, who will also be a major customer for the styrene produced.

Petrofina Canada Ltd. may build a styrene facility in Quebec. The company has a captive supply of benzene (currently most of this benzene is exported), access to ethylene from Gulf Canada Ltd.'s Varennes plant, and access to styrene technology from an affiliate in the United States. Petrofina could also obtain an extra low cost supply of ethylbenzene by expanding its xylenes separation facility.

A third possibility for a styrene plant is Monsanto Ltd. who need a



secure supply of the monomer for their styrene derivatives production. This plant could be built at either Montreal or Sarnia.

Until any of these possibilities are realized, there will be adequate styrene monomer production capacity to meet domestic requirements through 1985 from the new Polysar facility plus existing facilities.

Demand for styrene is estimated to be 170 Gg in 1977 and grow by about 8 % annually to 215 Gg/annum by 1980. Projections for 1985 and 1990 are 300 Gg/annum and 410 Gg/annum respectively, representing a growth rate of about 7 % from 1976-1990. A considerable export market must be found for any excess styrene production in the future. Polysar Ltd. plans to use surplus styrene production capacity to support their rubber, latex and plastics operations in The United States (10).

Table 8-23 summarizes the supply/demand forecasts for styrene and its derivatives from 1977 to 1990. A significant proportion of styrene derivatives will be imported over this period, probably from the United States.

A current practice of multinational companies is the use of swapping arrangements. An example of this is an arrangement that Polysar Ltd. has with B.A.S.F. in Germany. Polysar supplies styrene from Sarnia to a B.A.S.F. plant in Montreal and B.A.S.F. ships an equal amount from its plant in Ludwigshaven, Germany to a Polysar affiliate in France. Thus, each company saves delivery time and freight costs of shipping styrene to its overseas affiliates. This practice will probably become more widespread in the future, and may account for significant imports and exports of



TABLE 8-23

SUPPLY/DEMAND FORECASTS FOR STYRENEAND MAJOR DERIVATIVES

(All figures in Gg/annum)

	<u>1977</u>	<u>1980</u>	<u>1985</u>	<u>1990</u>
Styrene	170	215	300	410
Polystyrene	100	130	190	270
SB Rubber	100	110	130	145
SB Latex	40	45	64	82
ABS/SAN Resins	40	57	91	134
Unsaturated Polyester Resins	22	28	41	60
Imports (all polymers)	69	78	104	129



8-78

styrene and styrenic derivatives between the large companies in the United States and Canada.



8.7 CUMENE

8.7.1 INTRODUCTION

Cumene (isopropylbenzene, $C_6H_5CH(CH_3)_2$) is a member of the alkyl aromatic family of hydrocarbons. It is isomeric with several other compounds, such as normal propylbenzene, the ethyltoluenes, and the trimethylbenzenes.

Cumene is a volatile, refractive liquid which has a characteristic aromatic odor.

Cumene is a naturally occurring substance present in many crude oils, but the industrial product is manufactured from benzene and propylene. The major use of cumene is in the manufacture of phenol and acetone, and to a lesser extent as a component of motor fuels, particularly aviation gasoline (37), and in the manufacture of α -methyl styrene.

Cumene became important during World War II, as a component of aviation gasolines and helped greatly in increasing the 100-octane gasoline supplies during this period.

8.7.2 PRODUCTION, SOURCES AND USERS

Cumene is entirely produced by the catalytic alkylation of benzene by propylene. The most common catalysts for this reaction are aluminium chloride and solid phosphoric acid.

There is currently only one producer of cumene in Canada. This is the Gulf Oil Canada Company Ltd., of Montreal, Quebec with estimated capacity of 40-50 Gg/annum. This cumene is used captively by Gulf Oil to produce phenol and acetone. A flow chart of the commercial uses of cumene and



derivatives is presented in Figure 8-6. A similar flow chart for phenol, the major derivative of cumene, is presented in Figure 8-7.

Cumene is a naturally occurring constituent of crude oils. Thus it is present in most gasolines produced by oil refineries. The amount of cumene present in some gasoline blending streams of an Ontario refinery is presented in Table 8-5 (14). The amount of cumene in gasoline is not known, as this figure depends on the type of crude oil refined. However, it is believed to be no more than 0.1 % (38). Using the 1975 Canadian shipments figure for motor gasoline (16) of 35 G1, this would correspond to about 30 Gg of cumene present in this amount of gasoline. No commercially produced cumene is believed to be added to gasoline in Canada.

As there is presently only one producer of cumene in Canada, (Gulf Oil Canada, Montreal) Statistics Canada does not release production or uses figures for this chemical for reasons of confidentiality. However, based on the capacity of the Gulf Canada facility, current production is around 40 Gg/annum.

8.7.3 MARKET FORECAST

Gulf Oil of Canada Ltd., Montreal, at present the only manufacturer of cumene in Canada, may expand its facilities, but this expansion is planned for around 1985, so the impact would not be felt in the Canadian market for several years. Planned expansion is from the present 40-50 Gg/annum capacity to about 195 Gg/annum.

Key factors in the forecast for cumene production are the growth of domestic markets for phenol and acetone, and the ability to export cumene



FIGURE 8-6 USES OF CUMENE AND CUMENE DERIVATIVES

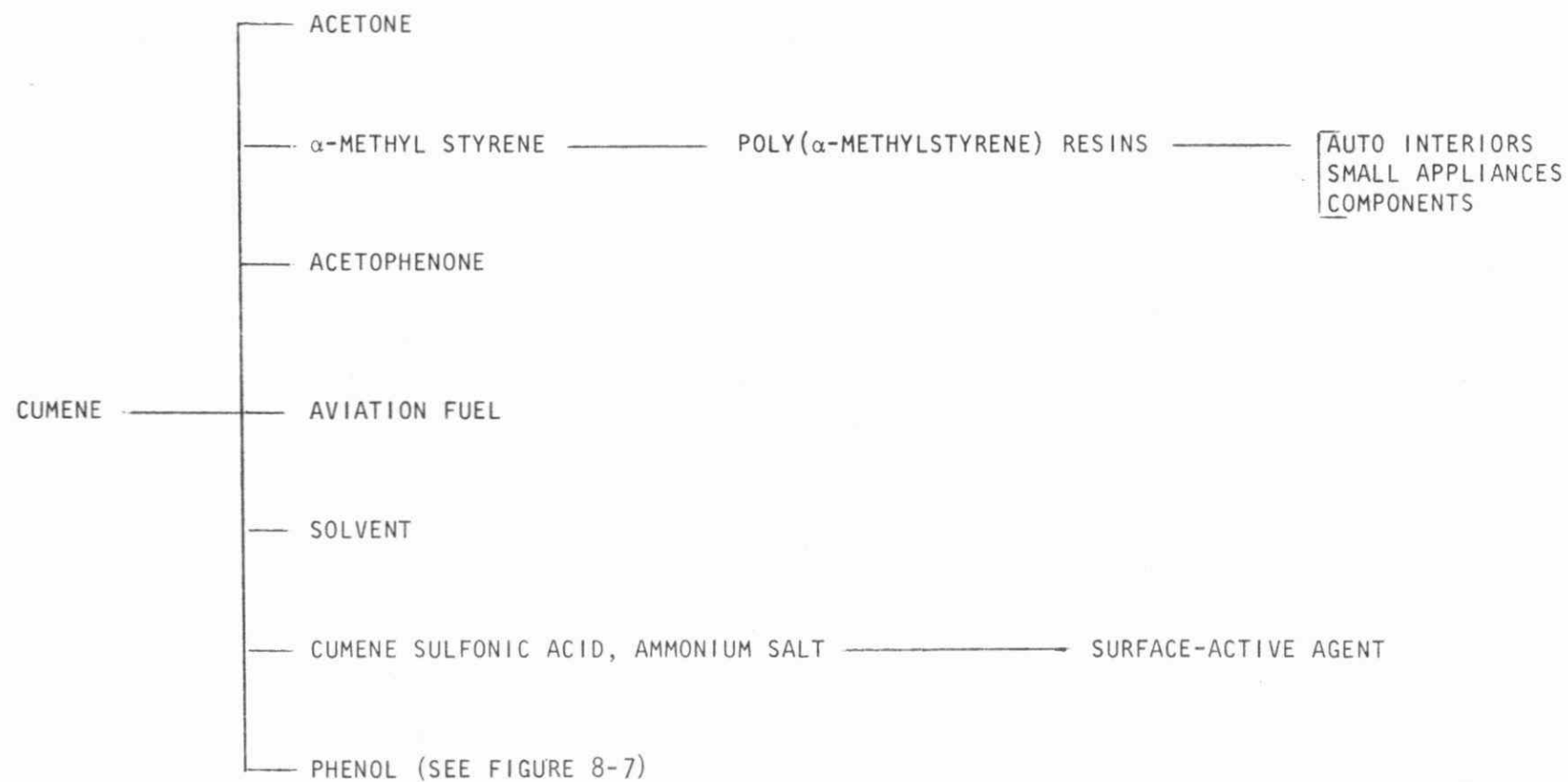
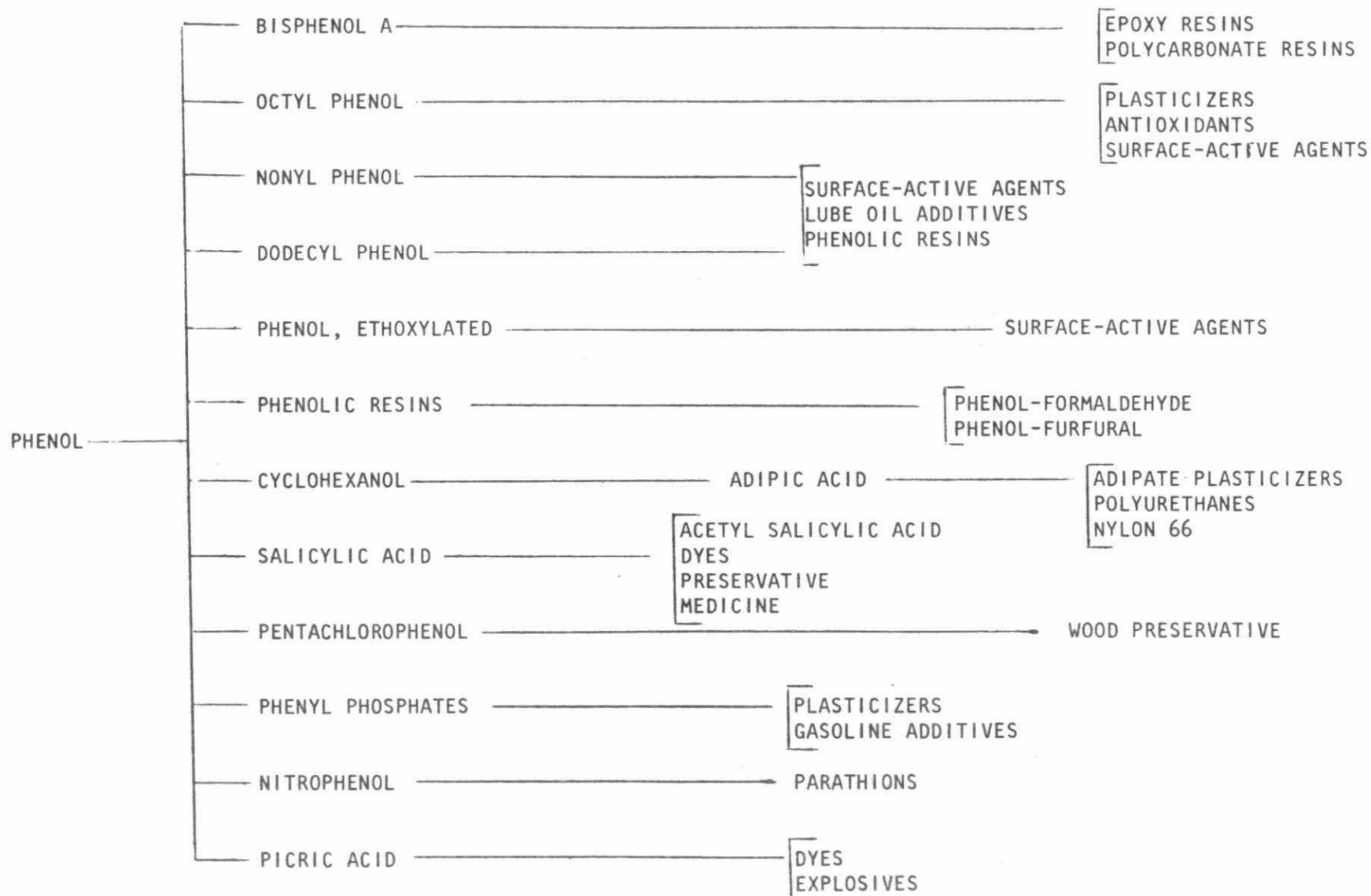




FIGURE 8-7 USES OF PHENOL AND DERIVATIVES



and/or phenol and acetone.

If a long term contract can be negotiated with a U.S. phenol producer, a cumene plant may be built in the Sarnia area (5).

Production forecasts for cumene are 40 Gg/annum in 1980 (essentially no change from 1977), 155 Gg/annum by 1985 (assuming a new 195 Gg/annum plant is built) and 185 Gg/annum by 1990.

There are no figures available to determine whether cumene is used in Canada to manufacture α -methylstyrene for plastics formulation. As only one plant currently exists for cumene manufacture, it is believed that no α -methylstyrene is produced in Canada, with all requirements for this chemical being met by imports.



8.8 NAPHTHALENE

8.8.1 INTRODUCTION

Naphthalene ($C_{10}H_8$) is an aromatic hydrocarbon with two ortho-condensed benzene rings. It is the first member of the series of condensed-ring aromatic compounds. Naphthalene is a white, crystalline solid having a characteristic "moth-ball" odor.

The principal uses for naphthalene are as a raw material for the production of phthalic anhydride, intermediates for synthetic dyes, insecticides, plasticizers and pharmaceuticals and in the production of the solvents tetrahydronaphthalene and decahydronaphthalene.

Naphthalene occurs in commercial concentrations in high-temperature coal tars and aromatized petroleum oil fractions. Naphthalene also occurs naturally in some essential oils.

8.8.2 PRODUCTION AND SOURCES

Until 1961, the commercial source of naphthalene in the U.S. was the tar obtained during the high-temperature coking of bituminous coal. After 1961, naphthalene was commercially recovered from petroleum refinery streams.

The impetus for naphthalene recovery from petroleum refinery streams came from increased demand for phthalic anhydride. Some phthalic anhydride plants could not use ortho-xylene as a feed-stock, and the increased cost of recovering large percentages of the naphthalene contained in coal-tar made the production and recovery of naphthalene from petroleum sources



profitable.

High-temperature bitumenous coal tar contains about 5-11 % of naphthalene, depending upon the temperature used and the length of coking time. The nature of the coal used for coking has very little influence. In the majority of by-product plants in the U.S., a tar containing about 10 % naphthalene is obtained. The tar is distilled and a fraction containing about 40 % naphthalene is used for processing.

Naphthalene generally is extracted from heavy reformat in refineries, usually by distillation.

There are only two suppliers of naphthalene in Canada. These are Record Chemical Co., Inc. with plants in Quebec and B.C., and Kent Laboratories Ltd., in Vancouver, B.C. It is believed that these companies import the naphthalene for distribution in Canada, or at most carry out a purification step.

Canadian coking operations produce a significant amount of coal tar. These operations produce about 10 gallons of tar per ton of coke (50 l/metric ton), of which about 10 % is naphthalene. This would correspond to about 25 Gg of naphthalene present in coal tar produced in Canadian coking operations in 1976 (5300 Gg of coke produced). The amount produced in Ontario in 1976 would be about 20 Gg, based on 80 % of Canadian facilities being located in Ontario (14). All of this coal tar is sold to Domtar Chemical Ltd., with plants in Sault Ste. Marie and Hamilton. This coal tar is put through a distillation step, mainly to separate out pitch. However, crude naphthalene is recovered at Domtar's



Hamilton plant. This naphthalene is shipped to the U.S. (for phthalic anhydride manufacture) (39). It is estimated that 10-15 Gg/annum of naphthalene is produced for this purpose.

There is no production of naphthalene from petroleum sources in Canada. However, naphthalene is a minor component of gasoline. It is believed to be present at concentrations up to the 1 % level. Based on 1975 figures for motor gasoline shipments of 35 G1, this would correspond to about 350 Gg of naphthalene present in gasoline produced in Canada and about 120 Gg used in Ontario during 1977.

8.8.3 USES OF NAPHTHALENE

Naphthalene is used in two industrial categories reported by Statistics Canada. These are manufacturers of industrial chemicals (organic) (SIC 3783) (16), who used 44 Mg in 1973 and 4.9 Gg in 1974, and miscellaneous chemical industries (SIC 3799) (17) who used 333 Mg in 1974 and 290 Mg in 1975. Total usage of naphthalene in 1975 amounted to 5.0 Gg (7).

Naphthalene was probably used in these industries to manufacture speciality chemicals such as insecticides, surfactants, and synthetic tanning agents, and in the manufacture of moth balls.

Figure 3-8 is a flow chart for the uses of naphthalene and derivatives in North America.

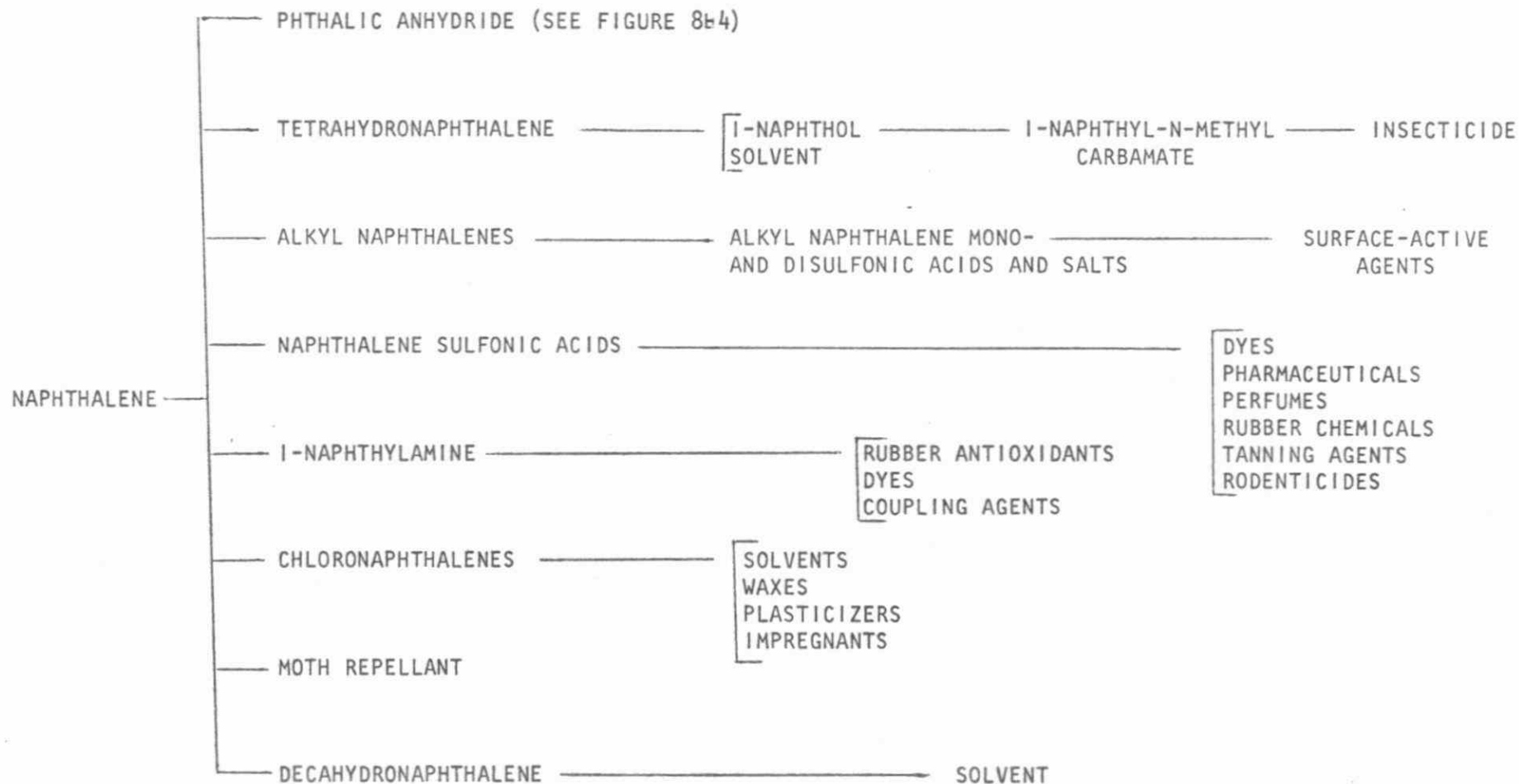
8.8.4 MARKET FORECAST

It is unlikely that naphthalene will be produced commercially in Canada in the near future. At the present time there is too little information on naphthalene usage in Canada and Ontario to see any kind of trend for future developments in the Canadian naphthalene market.





FIGURE 8-8 USES OF NAPHTHALENE AND NAPHTHALENE DERIVATIVES



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9 PROCESS DESCRIPTIONS



	SECTION	PAGE NO.
9	PROCESS DESCRIPTIONS	9-1
9.1	INTRODUCTION	9-4
9.2	PRODUCTION OF BENZENE, TOLUENE AND XYLENE (BTX)	9-6
9.2.1	Introduction	9-6
9.2.2	Hydrotreating	9-8
9.2.2.1	Feedstock	9-8
9.2.2.2	Process Description	9-8
9.2.2.3	Emissions/Discharges	9-10
9.2.3	Aromatics Extraction	9-11
9.2.3.1	Feedstock	9-11
9.2.3.2	Process Description	9-11
9.2.3.3	Emissions/Discharges	9-15
9.2.4	C6-C9+ Aromatics Separation	9-15
9.2.4.1	Feedstock	9-15
9.2.4.2	Process Description	9-15
9.2.4.3	Emissions/Discharges	9-17
9.2.5	Ortho-Xylene Separation	9-17
9.2.5.1	Feedstock	9-18
9.2.5.2	Process Description	9-19
9.2.5.3	Emissions/Discharges	9-19
9.3	PRODUCTION OF ETHYLBENZENE	9-20
9.3.1	Introduction	9-20
9.3.2.1	Feedstock	9-20
9.3.2.2	Process Description	9-20
9.3.2.3	Emissions/Discharges	9-23
9.4	PRODUCTION OF STYRENE	9-24
9.4.1	Introduction	9-24
9.4.2.1	Feedstock	9-24
9.4.2.2	Process Description	9-26
9.4.2.3	Emissions/Discharges	9-27
9.5	STYRENE POLYMERIZATION	9-29
9.5.1	Introduction	9-29
9.5.2	Production of Polystyrene	9-29
9.5.2.1	Feedstock	9-29
9.5.2.2	Process Description	9-29
9.5.2.2.1	Bulk Continuous Polymerization	9-31
9.5.2.2.2	Suspension Polymerization	9-31
9.5.2.3	Emissions/Discharges	9-32
9.5.3	Production of Styrene-Butadiene-Rubber (SBR) and Latex	9-33
9.5.3.1	Feedstock	9-33
9.5.3.2	Process Description	9-33
9.5.3.2.1	Cold Emulsion Polymerization	9-33
9.5.3.2.2	Hot Emulsion Polymerization	9-35
9.5.3.3	Emissions/Discharges	9-35



	SECTION	PAGE NO.
9.5.4	Production of Styrene-Acrylonitrile (SAN)	9-35
9.5.4.1	Feedstock	9-35
9.5.4.2	Process Description	9-36
9.5.4.3	Emissions/Discharges	9-36
9.5.5	Production of Acrylonitrile-Butadiene-Styrene (ABS)	9-36
9.5.5.1	Feedstock	9-36
9.5.5.2	Process Description	9-36
9.5.5.3	Emissions/Discharges	9-37
9.5.6	Production of Unsaturated Polyesters	9-37
9.5.6.1	Feedstock	9-37
9.5.6.2	Process Description	9-39
9.5.6.3	Emissions/Discharges	9-40
9.6	PRODUCTION OF PHTHALIC ANHYDRIDE.....	9-42
9.6.1	Introduction	9-42
9.6.2	o-xylene Oxidation Process	9-42
9.6.2.1	Feedstock	9-42
9.6.2.2	Process Description	9-42
9.6.2.3	Emissions/Discharges	9-44
9.7	COKING	9-50
9.7.1	Introduction	9-50
9.7.2	Manufacture of Coke	9-50
9.7.2.1	Feedstock	9-50
9.7.2.2	Process Description	9-50
9.7.2.3	Emissions/Discharges	9-52
9.8	COAL TAR DISTILLATION	9-57
9.8.1	Introduction	9-57
9.8.2	Coal Tar Distillation Process	9-57
9.8.2.1	Feedstock	9-57
9.8.2.2	Process Description	9-57
9.8.2.3	Emissions/Discharges	9-58
9.9	REFERENCES	9-59



9.1 INTRODUCTION

Although there are several industrial processes which either produce the aromatic compounds of interest in this report, or use them as a raw material, there are only a limited number of manufacturers using these processes in Ontario.

Only the processes used in Ontario are described in this section and include:

- 1) Benzene, Toluene and Xylene production from pyrolysis gasoline and catalytic reformat
- 2) Ethylbenzene production
- 3) Styrene production
- 4) Polymerization of styrene including
 - polystyrene
 - styrene-butadiene (SB) rubber and SB Latex
 - styrene-acrylonitrile (SAN)
 - acrylonitrile-butadiene-styrene (ABS)
 - unsaturated polyester
- 5) Phthalic Anhydride production
- 6) Coking
- 7) Coal Tar Distillation

For each process a description is given, and the areas where potential emissions and discharges may be expected are outlined. As in many cases only one or two companies are involved in producing a



particular product, it was not possible to obtain detailed information on the specific facilities. In these cases the processes are discussed in general terms based on information obtained from the literature.

Schematic diagrams showing the unit operations for selected processes are also included.



9.2 PRODUCTION OF BENZENE, TOLUENE AND XYLENE (BTX)

9.2.1 INTRODUCTION

Benzene, Toluene and Xylene (BTX) can be produced from either the by-products of the carbonization of coal, or from a petroleum base.

In Ontario, BTX production is from a petroleum base only. Two feedstocks may be processed:

- i) Catalytic reformat from petroleum refineries
- ii) Pyrolysis gasoline, a by-product of olefin production by thermal cracking

The processes involved in the production of BTX from each of the two feedstocks mentioned above are:

- hydrotreating
- aromatics extraction
- C_6 - C_{9+} aromatics separation
- toluene disproportionation/transalkylation
- hydrodealkylation of toluene
- C_8 aromatics fractionation
- para xylene crystallization
- para xylene adsorption
- C_8 aromatics isomerization

Figure 9-1 illustrates the flow scheme for these BTX processes.

It is believed that there is no benzene produced by the disproportionation/transalkylation or the hydrodealkylation of toluene in Ontario, and therefore these processes will not be discussed. The C_8 aromatics are treated only for the separation of ortho-xylene. The remaining C_8 mixed



aromatics are not separated further in Ontario. The discussion therefore will be limited to ortho-xylene separation and will not include para-xylene crystallization, para-xylene adsorption, or C_8 aromatic isomerization.

Each of the processes used in Ontario to produce BTX from catalytic reformat and pyrolysis gasoline is discussed below.

9.2.2 HYDROTREATING

9.2.2.1 FEEDSTOCK

Pyrolysis gasoline, which contains up to 80 % aromatics, and heated hydrogen are the materials entering the hydrotreating unit. An analysis for a typical pyrolysis gasoline is shown in Table 9-1 (1).

9.2.2.2 PROCESS DESCRIPTION

The hydrotreating unit is a catalytic hydrogenation process which saturates the diolefins and mono-olefins contained in the pyrolysis gasoline to obtain a stabilized mixed aromatics stream for input to the mixed aromatics extraction unit. The hydrogenation proceeds in two stages. The first stage is a low temperature process in which the fumeforming diolefins are saturated. The second stage hydrotreater is similar to the conventional refinery hydrotreater, and saturates the mono-olefins, and converts the sulfur and nitrogen compounds in the feed to H_2S and NH_3 .

A description of the steps involved in the hydrotreating process is as follows:



TABLE 9-1ANALYSIS OF TYPICAL PYROLYSIS GASOLINE

<u>COMPONENT</u>	<u>WT. % OF TOTAL HYDROCARBON</u>
Diolefins	15
Monolefins	8
Saturates	7
Benzene	32
Toluene	14
C ₈ Aromatics	11
C ₉₊ Aromatics	13
	<hr/> 100



- i) Hydrogen and pyrolysis gasoline are preheated by steam or by exchange with reactor effluent.
- ii) First stage liquid or gas-phase hydrotreating in a fixed-bed reactor, operated at 150-200 °C, using a nickel sulfide or platinum catalyst.
- iii) First stage effluent is heated in a furnace.
- iv) Second stage hydrotreating at a temperature between 300 °C and 400 °C using a cobalt-molybdenum catalyst.
- v) The second stage hydrotreater effluent is cooled using a water-cooled heat exchanger.
- vi) Cooled effluent from the second stage is fed to a gas-liquid separator. The hydrogen rich gas is recycled back to the hydrotreating process after being scrubbed with a caustic solution.
- vii) The liquid phase from the reactor is passed through a coalescer (water is used to trap coke particles formed in the pyrolysis reactor) and a stabilizer where light hydrocarbons are removed.

9.2.2.3 EMISSIONS/DISCHARGES

Gaseous emissions may be expected from the stabilizer-stripper section which separates dissolved NH_3 , H_2S and light hydrocarbons from the hydrotreated liquid. Some processes use hydrogen stripping and steam-air decoking to clean the first stage catalyst. This may produce gaseous emissions containing carbon monoxide.



Wastewater discharge from the process results from alkaline scrubbing of the hydrogen recycle stream, blowdowns, washing of the hydrotreated liquid to remove ammonium salts originating from hydrogenation of nitrogen compounds and coke particles from pyrolysis, and wash water from the coalescer.

Table 9-2 (1) shows the composition of a representative wastewater stream from a pyrolysis gasoline hydrotreating facility.

9.2.3 AROMATICS EXTRACTION

9.2.3.1 FEEDSTOCK

The stabilized liquid from the hydrotreating unit and/or catalytic reformates are the feedstock to the aromatic extraction unit. Typical compositions of the product from each unit are shown in Table 9-3.

9.2.3.2 PROCESS DESCRIPTION

One of two extraction processes may be used: UDEX or sulfolane. In both systems, the products from the extraction process are a mixed aromatics extract, and raffinate, which contains mainly paraffins.

The UDEX extraction process uses di-, tri- or tetra-ethylene glycol/water mixtures as the solvent. Extraction is conducted counter-currently in a trayed or rotating disc contactor. The solvent is separated from the aromatics in the extractor bottom by steam stripping, with the stripped aromatic vapor being condensed in an extract receiver. Both the extractor overhead (raffinate) and the extract are washed with water to recover traces of glycols. The wash water is treated in a water/solvent still and recycled, and the solvent is regenerated and recycled.



TABLE 9-2

CHARACTERISTICS OF WASTEWATER FROM TWO-STAGE
HYDROTREATING OF PYROLYSIS GASOLINE

<u>CHARACTERISTIC</u>	<u>CONCENTRATION</u>	<u>VOLUME OR WT. PER</u> <u>Mg OF PRODUCT</u>
Wastewater flow		0.114 m ³
Five day BOD	914 mg/l	0.10 kg
COD	2,755 mg/l	0.31 kg
TOC	306 mg/l	0.03 kg



TABLE 9-3

AROMATIC EXTRACTION FEEDSTOCK COMPOSITION

<u>CONSTITUENT</u>	<u>STABILIZED</u> <u>PYROLYSIS GASOLINE</u>		<u>REFORMATE</u> (1) vol. %
	Wt. %		
Benzene	37		5
Toluene	21		24
Ethylbenzene	6		4
Meta-, Para-xylene	4		13
Ortho-xylene	1		5
C ₉ and C ₁₀ Aromatics			4
Total Aromatics	69		55



A typical solvent to feed weight ratio is 20:1 for diethylene glycol, with the ratio increasing with an increase in the aromatic content of the feed.

A normal solvent make up requirement would be 0.9 g/m^3 of feed. The stripper steam ratio is on the order of 0.61. Temperatures which can be expected are: stripper bottom, 140°C ; extractor top, 140°C ; feed temperature, 115°C . The extractor pressure is approximately 860 kPa.

The sulfolane process uses tetrahydrothiophenedioxide ($(\text{CH}_2)_4\text{SO}_2$) as a solvent in a countercurrent extractor. A steam stripper under vacuum is used to separate the solvent from the hydrocarbons. The vapors from the stripper are condensed, and the hydrocarbons are separated from the aqueous solvent and recycled to the extractor. The stripper bottoms, containing the aromatics and aqueous solvent, are charged to an extract recovery column. The solvent from the recovery column is recycled and the extract is condensed from the extract recovery column overhead stream. Traces of solvent in the raffinate are washed with the water from the extract accumulator.

A typical solvent to feed ratio for the sulfolane process is 7:1, with a solvent make-up rate of 30 kg/Gg of feed. A stripper steam ratio of 0.13 by weight can be expected. Temperatures found in each unit are: stripper bottom, 140°C ; extractor top, 140°C ; feed temperature, 115°C . The extractor pressure is 207 kPa (1).



9.2.3.3 EMISSIONS/DISCHARGES

The major gaseous emissions are from process leaks.

Wastewater discharge containing oils can be expected from the condensate if steam ejection is used for generating a vacuum. One estimate suggests leaks in the heat exchanger may produce a COD content in the cooling water of 50-200 ppm. The total wastewater from the UDEX process is estimated at $0.504 \text{ m}^3/\text{Mg}$ of BTX extract, with a total organic carbon of 0.144 kg/Mg BTX extract produced.

In the solvent regeneration step, a sludge is produced which is normally deposited in a land fill site.

9.2.4 C₆-C₉+ AROMATICS SEPARATION

9.2.4.1 FEEDSTOCK

The aromatic extract produced from the aromatic extraction process is the feedstock to the C₆-C₉+ aromatics process.

The relative proportions of each aromatic are dependent on the source of the extract, ie whether it originated from pyrolysis gasoline, or from reformat. A typical composition for each feed is given in Table 9-4.

9.2.4.2 PROCESS DESCRIPTION

The extracted aromatics are separated into three fractions: Benzene, Toluene and mixed C₈+ aromatics. Separation is conducted in overhead refluxed fractionation columns. Before being fed to the column, the feed is heated and cleaned in clay towers. Approximately 0.6 kg of clay per m^3 of treated extract are used (1). The cleaning process removes



TABLE 9-4

AROMATICS SEPARATION FEEDSTOCK

<u>CONSTITUENT</u>	<u>SOURCE</u>	
	<u>PYROLYSIS GASOLINE</u> wt. %	<u>REFORMATE</u> vol. %
Benzene	54	9
Toluene	30	44
Ethylbenzene	9	7
Xylene	7	33
C ₉ and C ₁₀ Aromatics		7
	100	100



trace amounts of olefins and sulfur remaining after the aromatics extraction process.

Although information describing the operating conditions of the process is not available, the boiling points of the products are: benzene, 78.8 °C; toluene, 109 °C; C₈ Mixture, 137-142 °C, and C₉₊, 161-216 °C.

9.2.4.3 EMISSIONS/DISCHARGES

The major gaseous emissions, containing hydrocarbons, could be expected from intermittent release through relief vents. Pumps and valve seats are a source of fugitive emissions.

Spent clay from the cleaning towers, which may contain some olefin polymerization products, is a source of solid waste.

9.2.5 ORTHO-XYLENE SEPARATION

9.2.5.1 FEEDSTOCK

The feedstock to the separation unit is a mixture of aromatic C₈ isomers which can be obtained from the following sources:

- C₈₊ fraction of catalytic reformat extract
- C₈₊ fraction of pyrolysis gasoline extract
- equilibrium mixture from isomerization
- toluene disproportionation

In Ontario, only feedstocks from the first two sources are expected to be utilized in a new Sun Oil facility. Typical compositions of a feedstock is given in Table 9-5.



TABLE 9-5

ORTHO-XYLENE SEPARATION FEEDSTOCK COMPOSITION

<u>COMPONENT</u>	<u>SOURCE</u>	
	CATALYTIC REFORMATE EXTRACT	PYROLYSIS GASOLINE EXTRACT
	%	%
Ethylbenzene	22	53
Para-xylene	18	10
Meta-xylene	39	25
Ortho-xylene	22	12
	<hr/>	<hr/>
	100	100



9.2.5.2 PROCESS DESCRIPTION

Many processes separate both ortho-xylene and ethylbenzene from the C_8 aromatic mixture at this stage. However, facilities in Ontario will separate only the ortho-xylene from the mixture.

The ortho-xylene component is separated by fractional distillation, utilizing a 100 to 150 tray fractionation tower with a reflux ratio of 5-8 to 1. As the boiling point of ortho-xylene ($144.4^\circ C$) is the highest of the aromatic C_8 components in the feed mixture, the ortho-xylene is recovered from the bottom of the tower, and the remaining mixed C_8 aromatics are recovered from the top portion of the tower.

9.2.5.3 EMISSIONS/DISCHARGES

The major gaseous emissions containing hydrocarbons are from relief vents, and possibly fugitive emissions at valves and pump seals.



9.3 PRODUCTION OF ETHYLBENZENE

9.3.1 INTRODUCTION

Ethylbenzene can be produced by either the alkylation of benzene with ethylene, or by the fractionation of mixed xylenes. It is believed that no ethylbenzene is produced by separation of the mixed aromatics in Ontario.

The two major alkylation processes are the Alkar process, and the Friedel-Crafts Alkylation process. Most of the ethylbenzene in North America and Europe is produced by the Friedel-Crafts method, using an aluminum chloride catalyst, and it is believed to be the process used by the two producers in Ontario. This process is illustrated schematically in Figure 9-2.

9.3.2.1 FEEDSTOCK

The input materials to the alkylation process are ethylene, recycled benzene, fresh benzene, and aluminum chloride catalyst. The products from the process include: ethylbenzene, benzene and polyethylbenzenes, with the composition of the product dependent on the ratio of the ethylene/benzene in the feed. Typically a ratio of 0.5-0.6 is used, which produces a product containing 46 % ethylbenzene, 42 % benzene, 10 % diethylbenzene, and 2 % higher molecular weight products (2).

9.3.2.2 PROCESS DESCRIPTION

The following steps are used in the production of ethylbenzene by the alkylation of benzene using the Friedel-Crafts process:



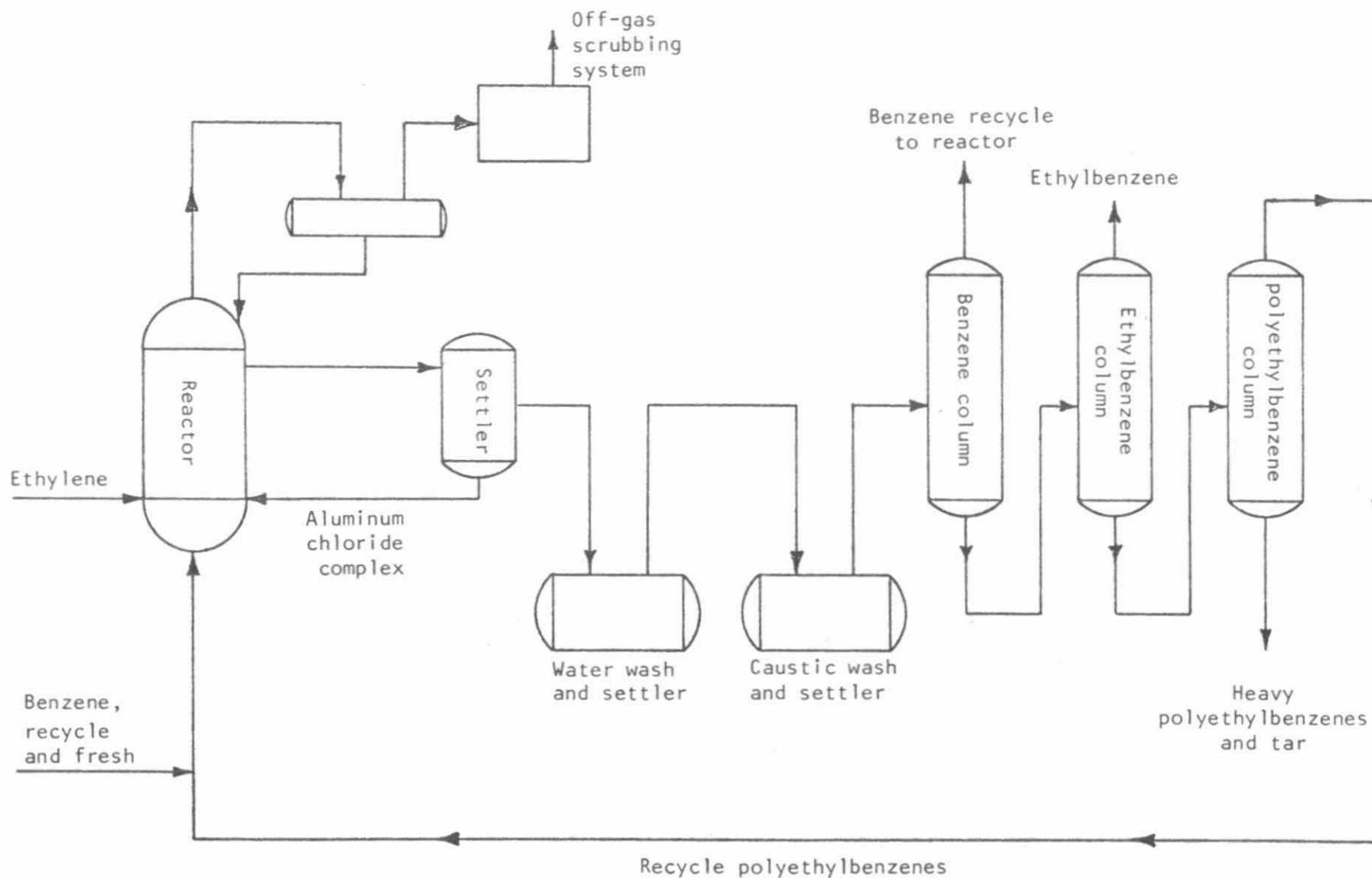


FIGURE 9-2

ETHYLBENZENE MANUFACTURE EMPLOYING ALUMINUM CHLORIDE AS CATALYST (2)

- i) Ethylene, fresh and recycled benzene, recycled polyethylbenzenes and the aluminum chloride catalyst are fed to the bottom of the reactor.
- ii) The vessel is filled to approximately 10.5 m, with the reactants overflowing through a pipe at the top of the reactor. The temperature is maintained at the boiling point of the mixture (80-100 °C) at atmospheric pressure.
- iii) Gaseous products, which include benzene, hydrogen chloride and inerts, leave the reactor at the top, and enter a condenser.
- iv) Benzene, captured in the condenser, flows back to the reactor. The non-condensed gases are scrubbed with a polyethylbenzene absorbent for trace benzene removal, and washed with water for HCl removal.
- v) Liquid products flow from the reactor, are cooled, and sent to settlers where the aluminum chloride complex is removed and returned to the reactor.
- vi) Alkylate passes through a water wash to break any residual complex and then to a 20 % caustic wash to neutralize the alkylate.
- vii) The washed alkylate enters a series of 3 distillation columns. The first removes benzene, the second the ethylbenzene and the third lighter polyethylbenzenes as overheads. The bottom fraction of the third



column contains heavy polyethylbenzenes and tar.

viii) Both the benzene from the first column and the light polyethylbenzenes are recycled to the reactor.

9.3.2.3 EMISSIONS/DISCHARGES

Off gases from the scrubbing system are a potential source of emissions. However, they are often compressed and used as fuel.

Wastewater discharge includes scrubber effluent, separator effluents, and waste from the dealkylation unit.

Quantities of waste which have been reported (4) are:

	per metric ton of product	total waste per annum for production of 210 Gg/annum
Scrubber Effluent - benzene -	11.00 kg	2.31 Gg
HCl -	3.85 kg	0.81 Gg
Separator Effluent - aluminum salts-trace		
sodium hydroxide		
& sodium chloride -	1.90 kg	0.40 Gg
Dealkylation Unit - aluminum salts -	7.05 kg	1.48 Gg
tarry matter -	21.55 kg	4.53 Gg



9.4 PRODUCTION OF STYRENE

9.4.1 INTRODUCTION

Styrene can be produced by a number of techniques. Processes which have been used or considered for commercial production include:

- i) Dehydrogenation of ethylbenzene.
- ii) Oxidative conversion of ethylbenzene to α -phenylethanol via acetophenone and subsequent dehydration of the alcohol.
- iii) Side chain chlorination of ethylbenzene followed by dehydrochlorination
- iv) Side chain chlorination of ethylbenzene, hydrolysis to the corresponding alcohols, followed by dehydration
- v) Pyrolysis of petroleum and recovery from various petroleum processes
- vi) Oxidation of ethylbenzene to ethylbenzene hydroperoxide which is reacted with propylene to give α -phenylethanol and propylene oxide. The alcohol is then dehydrated to styrene.

The two producers of styrene monomer in Ontario use the dehydrogenation of ethylbenzene process. This process is illustrated schematically in Figure 9-3.

9.4.2.1 FEEDSTOCK

The two components fed to the dehydrogenation reactor are ethylbenzene and steam.



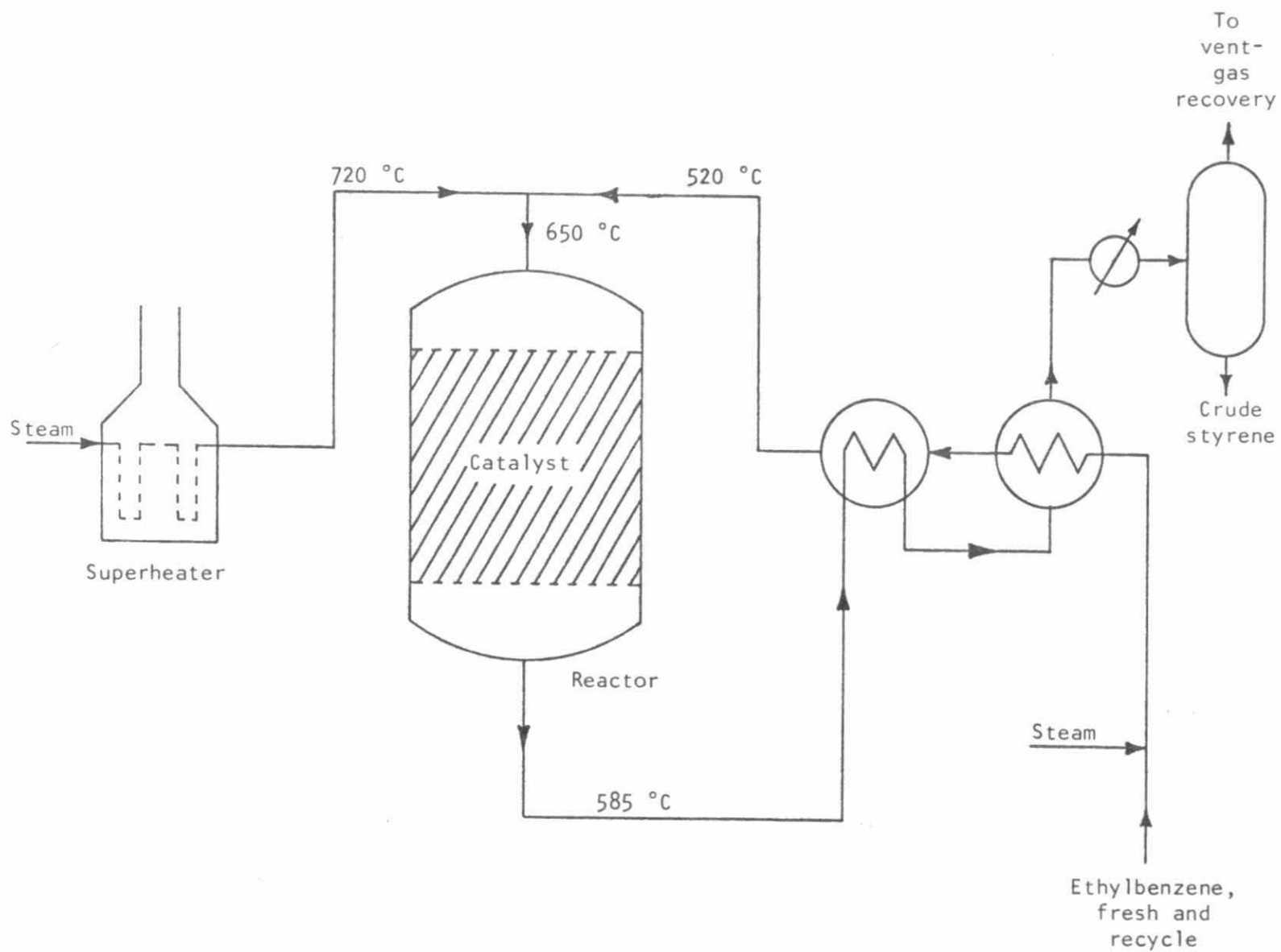


FIGURE 9-3

STYRENE MANUFACTURE BY ADIABATIC DEHYDROGENATION OF ETHYLBENZENE (2)

9.4.2.2 PROCESS DESCRIPTION

Styrene is manufactured by the direct dehydrogenation of ethylbenzene. The processes in Ontario use the adiabatic cracking process. Feed to the reactor consists of an ethylbenzene-steam mixture, entering the reactor from the top at approximately 650 °C.

Steps involved in the process are as follows:

- i) Liquid ethylbenzene, fresh and recycled, is mixed with approximately 10 % of the steam. The ethylbenzene/steam mixture is heated to 520-550 °C by heat exchange with reactor product.
- ii) The remaining steam is superheated in a fixed heater to approximately 720 °C.
- iii) The superheated ethylbenzene and superheated steam is mixed and fed to the top of the reactor at about 650 °C.
- iv) The gases pass through the reactor, passing through a bed of catalyst, usually iron oxide pellets.
- v) Effluent leaves the reactor at approximately 585 °C, and is cooled by the heat exchanger (see (i) above) and then condensed in a series of condensers.
- vi) Vent gases pass through a scrubber to remove organics, and water is removed from the effluent in a separator.
- vii) The crude styrene is purified by a series of vacuum distillation columns. Vacuum is used in order to reduce operating temperatures, and thus minimize



the polymerization of the styrene.

- viii) Often three towers are used: the first separates benzene and toluene; the second separates ethylbenzene; the third separates the styrene from tar and polymers. In the third column the styrene is removed from the top, and the tar and polymers are taken off the bottom of the tower.

9.4.2.3 EMISSIONS/DISCHARGES

The amount of wastewater discharge is variable depending on the method used to obtain the vacuum in the distillation columns. This vacuum can be produced by using either a barometric condenser or a surface heat exchanger in conjunction with steam jets. However, significantly more water effluent will be generated if a barometric condenser is used.

The following shows the effluent characteristics of the two cases. Plant 1 uses a barometric condenser, Plant 2 uses a surface heat exchanger. In both cases, liquid waste from the separator and scrubber are included (3).

	Plant 1	Plant 2
Flow	23.4 l/kg	5.5 l/kg
COD	219 mg/l	426 mg/l
BOD ₅	69 mg/l	70 mg/l
TOC	22 mg/l	22 mg/l

Approximately 7.0 kg of residue per Mg of styrene is taken from



the bottom of the third distillation column (4). The residue contains styrene trimer, stilbene, biphenylnaphthalene, phenanthrene and ethylphenanthrene.

Gaseous emissions are minimal, possibly occurring around valves and pump seals.



9.5 STYRENE POLYMERIZATION

9.5.1 INTRODUCTION

Styrene is used extensively as a monomer in the production of a number of plastics. Products produced in Ontario from styrene include: polystyrene, styrene-butadiene rubber (SBR), styrene-butadiene latex, acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN) and unsaturated polyesters. A very small amount of the styrene produced is used in solvent applications for styrene polymers.

The polymerization processes used to produce the polymers listed above will be described in the following section.

9.5.2 PRODUCTION OF POLYSTYRENE

9.5.2.1 FEEDSTOCK

Styrene is the major feed. If a solvent is used, it is normally ethylbenzene.

9.5.2.2 PROCESS DESCRIPTION

Polystyrene is produced by the polymerization of styrene. The two most common processes for producing polystyrene are the bulk continuous and suspension processes.

It is believed that either or both of these processes are used by the two Ontario producers.

A description of each process is given below. The bulk continuous process is illustrated schematically in Figure 9-4.



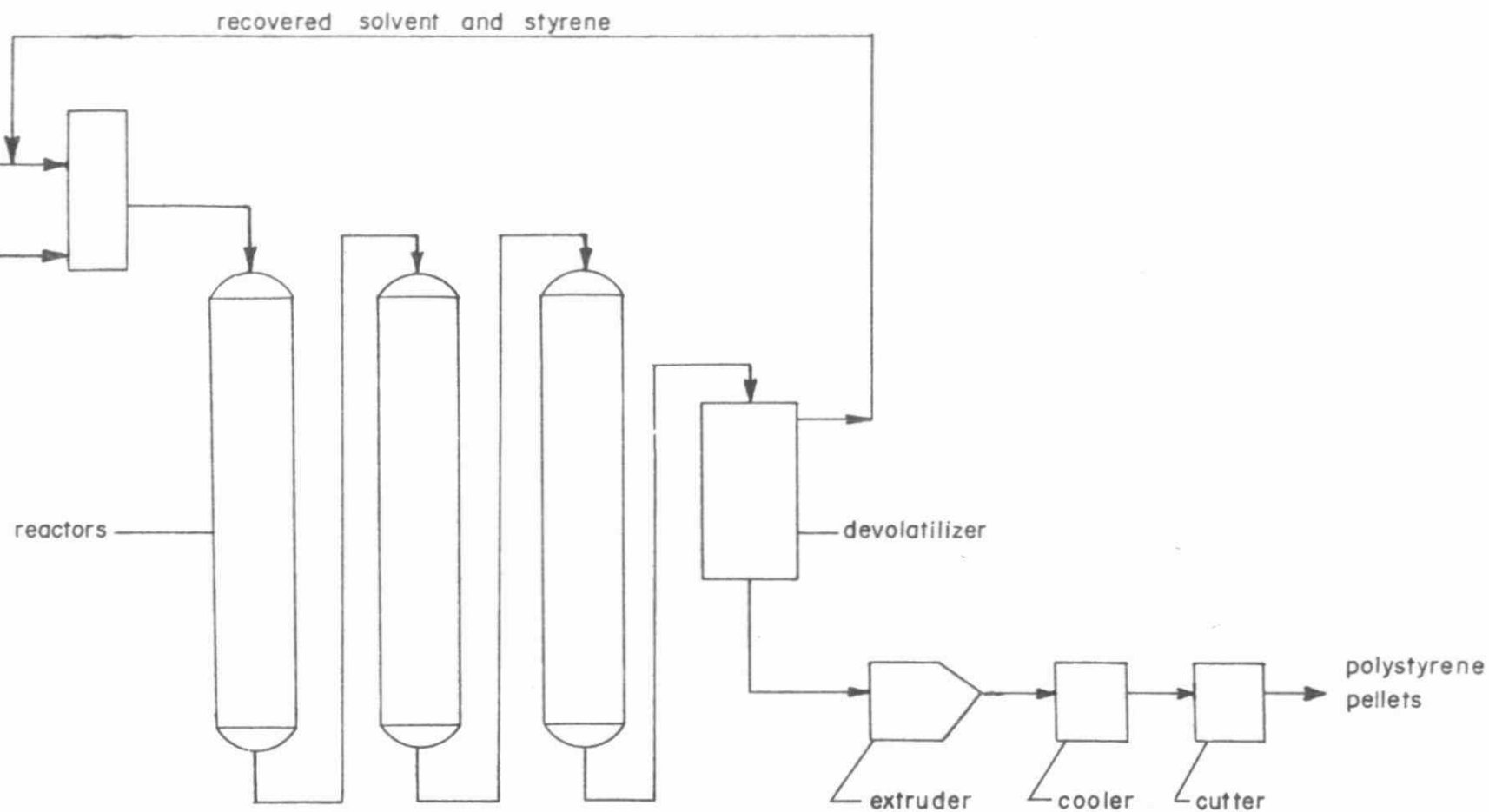


FIGURE 9-4

CONTINUOUS SOLVENT PROCESS FOR STYRENE POLYMERIZATION (5)

9.5.2.2.1 BULK CONTINUOUS POLYMERIZATION

The continuous process can be used either with or without a solvent. If a solvent is used, 5-25 % ethylbenzene is mixed with the styrene, along with other additives, before entering the first stage. Approximately 1.1 kg of styrene is required per kg of product (4).

In a process utilizing three reactors, the first reactor is maintained at 110-130 °C, and the temperature of the solution increased until the last reactor, where the temperature is 150-170 °C. The solution is pumped from the last reactor to a devolatilization tank kept at a low pressure and 225-250 °C, where the unreacted monomer and solvent are flashed off, condensed, and returned to the styrene/solvent mixing tank (5).

The hot polystyrene is further processed by extrusion, pelletizing, coloration, mixing and plasticizing.

9.5.2.2.2 SUSPENSION POLYMERIZATION

In the manufacture of general purpose polystyrene by the suspension process, water is the most common suspending medium. Due to the large amount of water required, a batch process is used. The reaction vessel is filled with the desired amount of hot water containing tricalcium phosphate (TCP), and the monomer is then added to the polymerization vessel. Approximately 1.025 kilograms of styrene are required per kilogram of product. Typical water to monomer ratios are 1:1 to 3:1 (5). Additives such as plasticizers, catalysts, or initiators are weighed and added directly to the suspension polymerization vessel. Polymerization



is completed by raising the temperature in the vessel from 90 °C to 115 °C and then to 130 °C over a period of 8 to 10 hours (5).

Upon completion of polymerization, the material is flushed from the reactor into a holding tank from which it is fed to a centrifuge which separates the TCP from the polymer beads. The beads are dried, extruded, cooled, chopped and packaged. Types of dryers used include rotary, co-current air driers, counter-current steam-tube driers and rotary vacuum driers.

9.5.2.3 EMISSIONS/DISCHARGES

Potential sources of emissions from the bulk continuous process are at the polymerization reactor, devolatilizer, monomer recovery unit and extrusion equipment. Emissions are most likely to occur during process interruption. An estimate for the total styrene loss is approximately 2 % or 21.8 kilograms per metric ton (4). For a total polystyrene production of 135 Gg per annum, this represents an annual loss of 2.9 Gg. This figure is based on 245 Gg per annum of styrenic polymers produced with 55 % of this polymer production being polystyrene.

The principal potential emission source from the suspension polymerization process is from the drier. The concentration of monomer is low, but a very high volume is used.

Other potential sources include: leaks from storage and reaction vessel, filling and dumping of reactor vessel, washing, centrifugation, and vents from the extruder.



9.5.3 PRODUCTION OF STYRENE-BUTADIENE-RUBBER (SBR) AND LATEX

9.5.3.1 FEEDSTOCK

The major ingredients in styrene-butadiene polymerization are styrene and butadiene.

9.5.3.2 PROCESS DESCRIPTION

Styrene-butadiene can be polymerized to form either a rubber compound or a latex. Either the cold emulsion polymerization or the hot emulsion polymerization process is used. It has been found that the cold process gives a superior product and is the process most often used. This process is illustrated schematically in Figure 9-5.

The same basic process is used to make both the rubber and the latex.

The major difference occurs after polymerization. For dry rubber compounding, the latex is coagulated, dried, and used in the solid state. Latex compounding, on the other hand, is done in the liquid state, and the compounded liquid latex is used directly to produce commercial articles without first converting to a solid.

A brief description of the polymerization processes follows.

9.5.3.2.1 COLD EMULSION POLYMERIZATION

In the cold emulsion process, styrene and butadiene are premixed at approximately 5 °C in an aqueous soap solution. Free radicals are generated by adding a sodium formaldehyde sulfoxylate recipe initiating free radical polymerization.



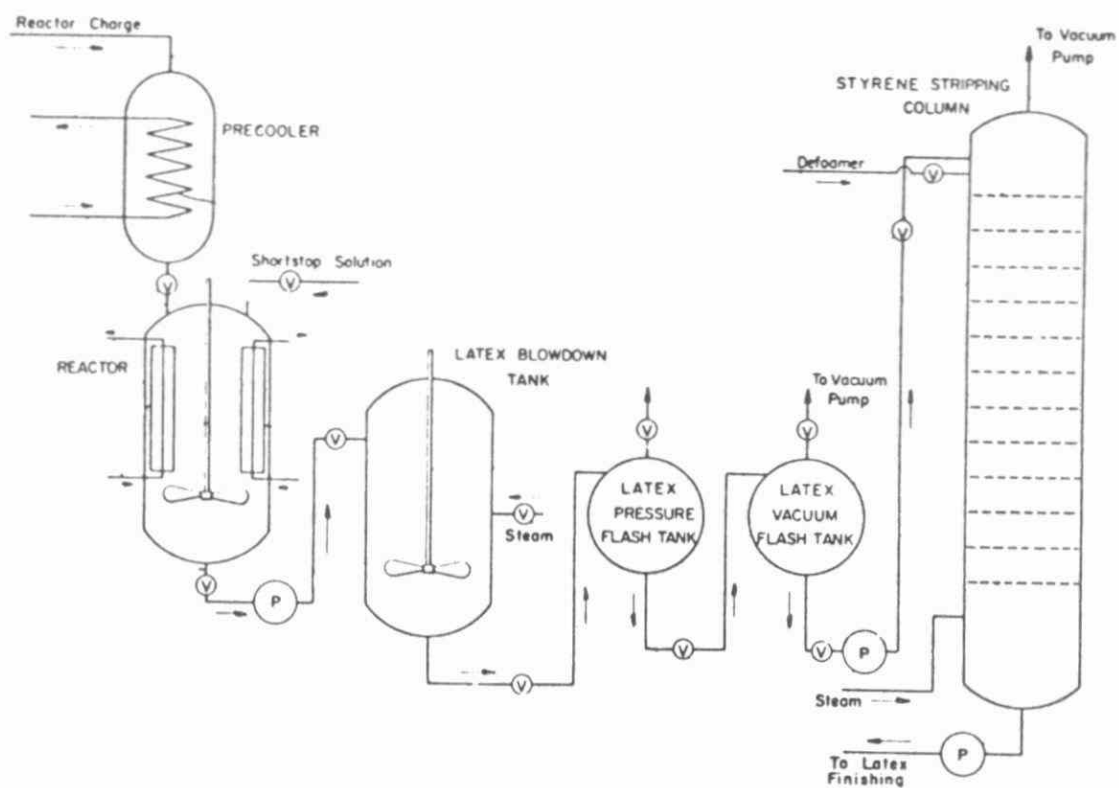


FIGURE 9-5

STYRENE-BUTADIENE MANUFACTURE (9)

The solution is pumped to a number of reactor vessels in series, each held at 5 °C. The polymerization is terminated at 60 % conversion in a tubular reactor by the addition of chain-terminating agents such as hydroquinone. The copolymer product is typically composed of 77 % butadiene and 23 % styrene.

The polymer emulsion is steam stripped to remove the unreacted monomer, coagulated with a brine acid solution, washed, and dried.

9.5.3.2.2 HOT EMULSION POLYMERIZATION

This process is similar to the cold process except that a different initiator system is used, and the reaction temperature is maintained at 50 °C.

9.5.3.3 EMISSIONS/DISCHARGES

The primary source of discharge is the caustic wash of butadiene to remove inhibitors. The waste water contains sodium hydroxide and inhibitors. The waste stream from the drying section contains catalyst residue, sodium chloride and emulsifying agents (4).

No information was available on sources or amounts of gaseous emissions.

9.5.4 PRODUCTION OF STYRENE-ACRYLONITRILE

9.5.4.1 FEEDSTOCK

Approximately 260 kilograms of acrylonitrile and 746 kilograms of styrene is required to make one metric ton of product.



9.5.4.2 PROCESS DESCRIPTION

SAN resins are produced by mass polymerization in a batch process. Acrylonitrile and styrene are mixed with ethylbenzene, which is used as a rate modifier, in the reactor. The temperature in the reactor is maintained between 148 and 152 °C.

9.5.4.3 EMISSIONS/DISCHARGES

The most significant emission occurs when the reaction and equipment are purged with nitrogen. Trace amounts of acrylonitrile and styrene escape with the nitrogen.

9.5.5 PRODUCTION OF ACRYLONITRILE-BUTADIENE-STYRENE (ABS)

9.5.5.1 FEEDSTOCK

The following amounts of feed materials are required to produce one metric ton of product (4).

Styrene	175 kg
Acrylonitrile	75 kg
Polybutadiene	250 kg
SAN resin	495 kg

9.5.5.2 PROCESS DESCRIPTION

ABS resin is manufactured using a batch process. A polybutadiene latex is fed to a back reactor, normally a standard jacketed 14,000 litre vessel. Acrylonitrile and styrene are mixed in a monomer mix tank and then fed to the reactor at a rate such that the temperature is maintained at 60 °C. The reaction is normally 95 % complete at the



end of five hours. The ABS resin is coagulated and separated from the water (5). Figure 9-6 is a schematic illustration of an ABS manufacturing process.

9.5.5.3 EMISSIONS/DISCHARGES

The major sources of waste are from the steam stripper in the resin recovery system and a water wash on the rotary filter which separates coagulated resin from the water. The waste which may be expected from each source is as follows (4):

Steam Stripper Wash

styrene	trace
acrylonitrile	trace
graft resin	8.8 kg/Mg
calcium chloride	1.4 kg/Mg

Rotary Filter Water Wash

styrene	0.2 kg/Mg
acrylonitrile	0.5 kg/Mg
sulfuric acid (98 %)	0.5 kg/Mg
sodium bisulfite	0.2 kg/Mg
calcium chloride	0.2 kg/Mg

A trace of acrylonitrile may be emitted from the steam stripper and decanter in the acrylonitrile recovery section.

9.5.6 PRODUCTION OF UNSATURATED POLYESTERS

9.5.6.1 FEEDSTOCK

The major input materials are, dihydric alcohols, unsaturated dibasic



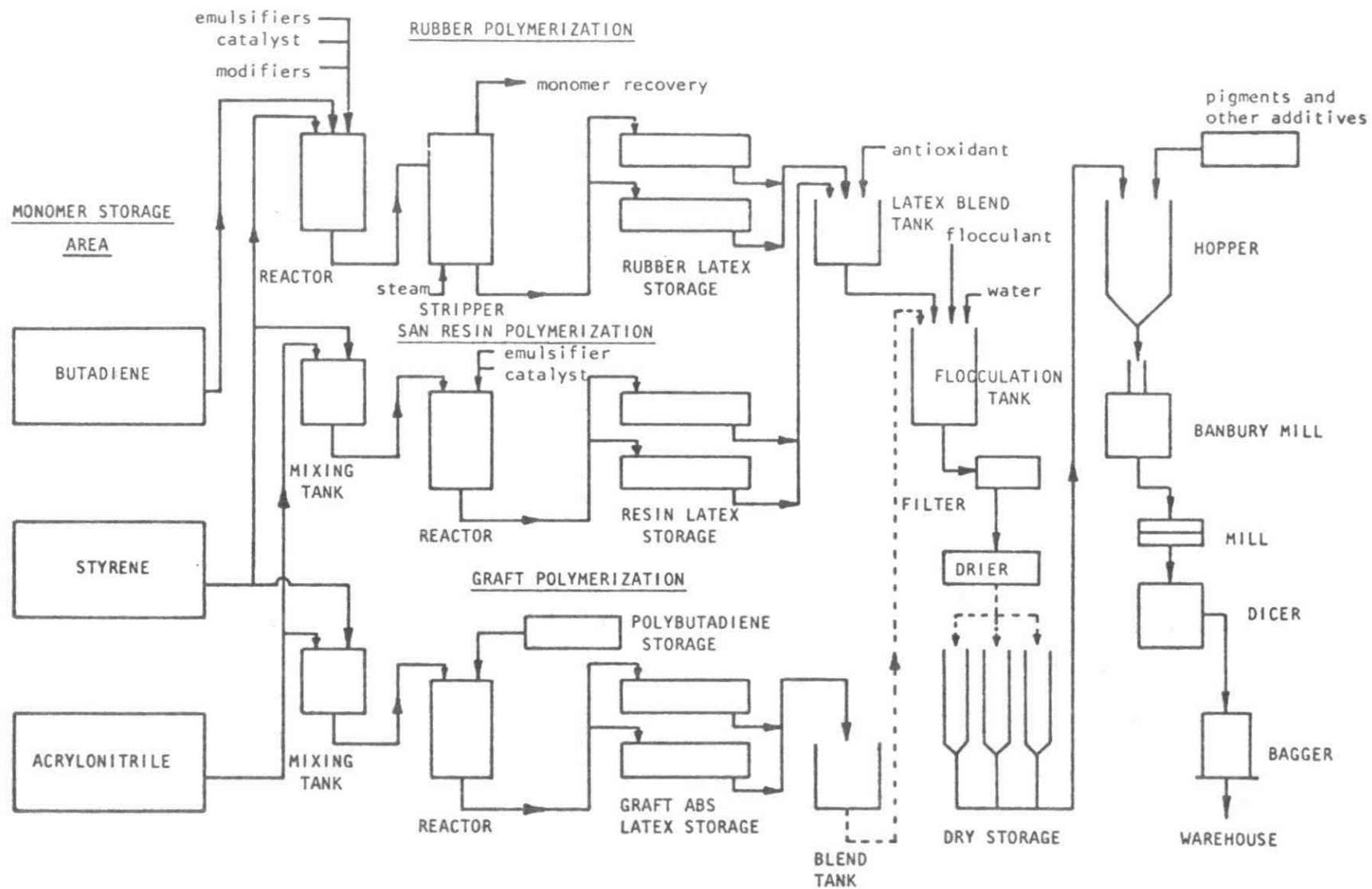


FIGURE 9-6

FLOW CHART FOR ABS MANUFACTURE (5)

acids or anhydrides and an unsaturated monomer, such as styrene.

9.5.6.2 PROCESS DESCRIPTION

Unsaturated polyesters are manufactured by esterifying unsaturated dibasic acids or anhydrides with dihydric alcohols. The unsaturated prepolymers are dissolved in an unsaturated monomer such as styrene, which acts as the cross linking agent to form the desired polymer.

The process is a high temperature batch operation. The esterification ingredients, dibasic acids or anhydride, usually phthalic anhydride or isophthalic acid and maleic anhydride, fumaric acid, or succinic acid, are reacted at 190-220 °C with polyhydric alcohols such as propylene glycol, ethylene glycol, or diethylene glycol, for 8-20 hours. During esterification an inert gas may be sparged through the mixture to remove water formed during condensation.

When the esterification has progressed to the desired stage, the reaction mixture is cooled to 100-150 °C and sent to a thinning tank which contains the monomer used to cross-link the polyester, and the inhibitors. The most common cross-linking agent used is styrene. Normally an excess of 30-40 percent of styrene is used. An excess is required to ensure that most of the maleic unsaturated groups are reacted and optimum strength is achieved. The styrene monomer will polymerize not only with an active maleic radical but also with an active styrene radical. Maleic radicals, however, will react only with styrene monomer. Common inhibitors used are hydroquinone or para-tertiary-butylcatechol.



When the cross-linking has been completed the solution is filtered and sent to storage (5).

Figure 9-7 is a schematic illustration of an unsaturated polyester manufacturing process.

9.5.6.3 EMISSIONS/DISCHARGES

The main areas of possible emissions are:

- vapor escaping through packing on reactor and thinning tank stirring equipment
- vapor escaping through vents on reactor and thinning tank
- vapor escaping in the raw material storage area and in drumming areas



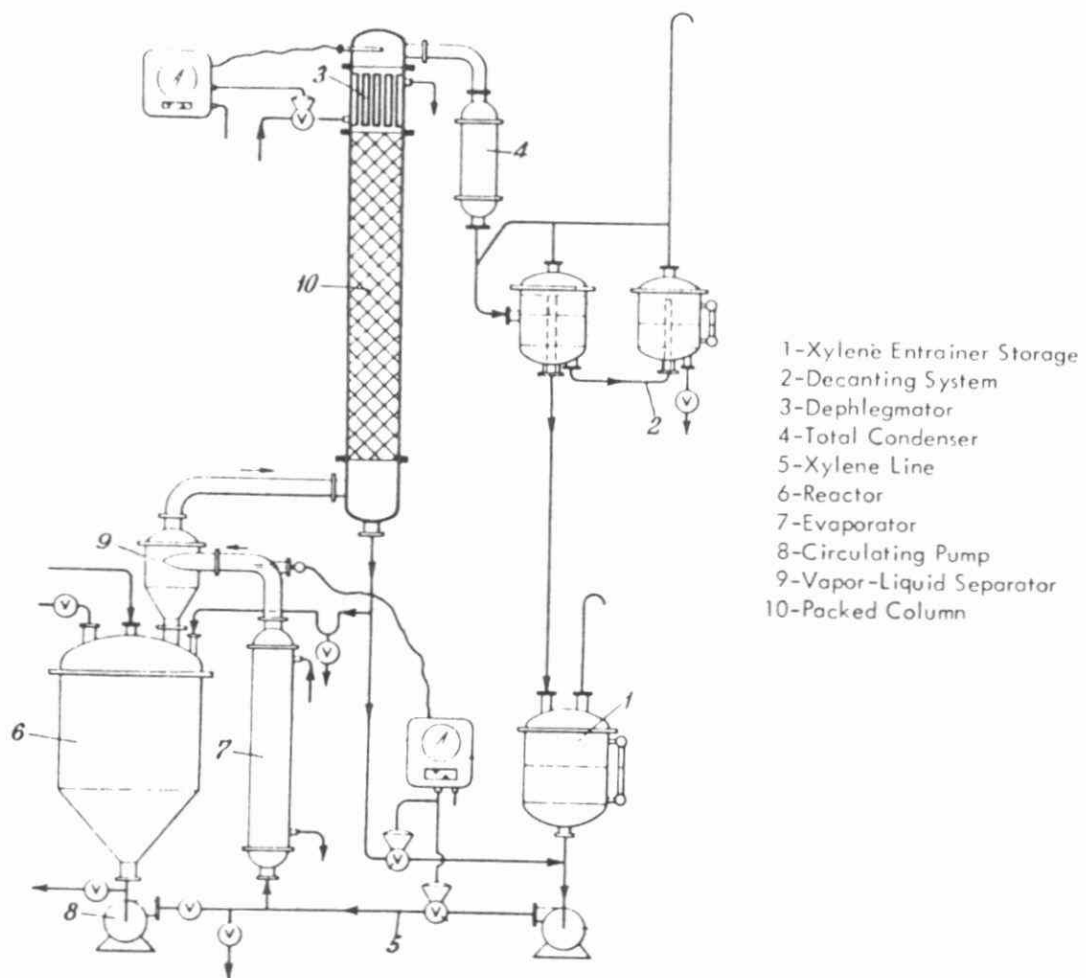


FIGURE 9-7

MANUFACTURING PROCESS FOR UNSATURATED POLYESTERS (9)



9.6 PRODUCTION OF PHTHALIC ANHYDRIDE

9.6.1 INTRODUCTION

Phthalic anhydride is produced by the oxidation of either naphthalene by the Badger-Sherwin-Williams process, or ortho-xylene by the BASF process. At the present time, there is only one producer of phthalic anhydride in Ontario, and this manufacturer uses ortho-xylene as the feedstock to a BASF phthalic anhydride process. As it was not possible to obtain information on the facility in Ontario, a general description of the BASF o-xylene oxidation process is given.

9.6.2 O-XYLENE OXIDATION PROCESS

9.6.2.1 FEEDSTOCK

To produce one kilogram of phthalic anhydride, approximately 1.02 kilograms of o-xylene and 5.87 kilograms of oxygen are required. Oxygen is provided by using compressed air.

The synthesis of phthalic anhydride is by the oxidation of o-xylene in the gas phase. The reaction takes place in a fixed bed reactor using a vanadium pentoxide catalyst, at a temperature of 350-385 °C.

9.6.2.2 PROCESS DESCRIPTION

Filtered air is compressed and preheated to a temperature of 149 °C using steam. The liquid xylene is injected into the air stream and is vaporized. An excess of air is used to maintain the xylene mole fraction below its lower explosive limit (1.5 % by volume in air). Approximately 0.5 % to 2.5 % by weight of sulfur dioxide is added to



the feed stream to maintain catalyst activity. Unvaporized feed is removed and the reactants fed to the fixed bed reactor. All of the xylene is oxidized, approximately 80 % to phthalic anhydride, and 20 % to oxidation by-products.

The process vapors leave the reactor at approximately 375 °C, pass through the waste heat boiler, and into a switch condenser to separate crude phthalic anhydride and by-products from the process air.

Due to the excess (567 %) of air used, the partial pressure of the phthalic anhydride in the reactor effluent is such that the dewpoint is below its melting point. Hence the product condenses as a solid. In order to obtain the phthalic anhydride in a liquid state, a switch condenser is used.

A switch condenser is a tubular condenser which is alternately heated and cooled by separate heat transfer oil streams on an automatically controlled cycle. During the cooling cycle, the phthalic anhydride crystallizes on the outer surface of finned tubes within the condenser. During the heating cycle, the solid phthalic anhydride is melted and then transferred to the crude product storage tank. A typical operation (6) uses a sequence of nine individual condensers with six condensing and two melting at any given time. The ninth unit is on standby to allow for periodic maintenance without shut-down.

The crude phthalic anhydride (99 % - 99.5 %) is stored at 149 °C at atmospheric pressure. This crude phthalic anhydride is refined in two steps; heat treatment followed by vacuum distillation. Heat



treatment allows the evaporation of water, maleic anhydride and benzoic acid through a vacuum jet ejector exhaust system. The distillation operation consists of a stripping column and a rectifying column. Phthalic anhydride (99.99 %) is the overhead fraction of the column. It is condensed and taken to storage. The bottom of the column is normally taken to an incinerator for disposal.

The BASF process for manufacturing phthalic anhydride from o-xylene is illustrated schematically in Figure 9-8. Table 9-6 identifies the numbered process streams.

9.6.2.3 EMISSIONS/DISCHARGES

The primary waste stream is the off gas from the switch condenser. Control of emissions is by incineration and/or scrubbing. Potential emission sources from jet ejectors and the vacuum lines from the stripper and rectifying column of the distillation process are normally fed to the main emission control device.

Other potential sources of emission are:

- storage tank vent gases
- scrubber vent gas
- flaker and bagging vent gases
- fugitive emissions

For a typical 5.9×10^4 metric tons per year plant, 7,400 kg/hr of xylene is required to make 7,300 kg/hr of phthalic anhydride. Contaminants in the switch condenser off-gas include (6):



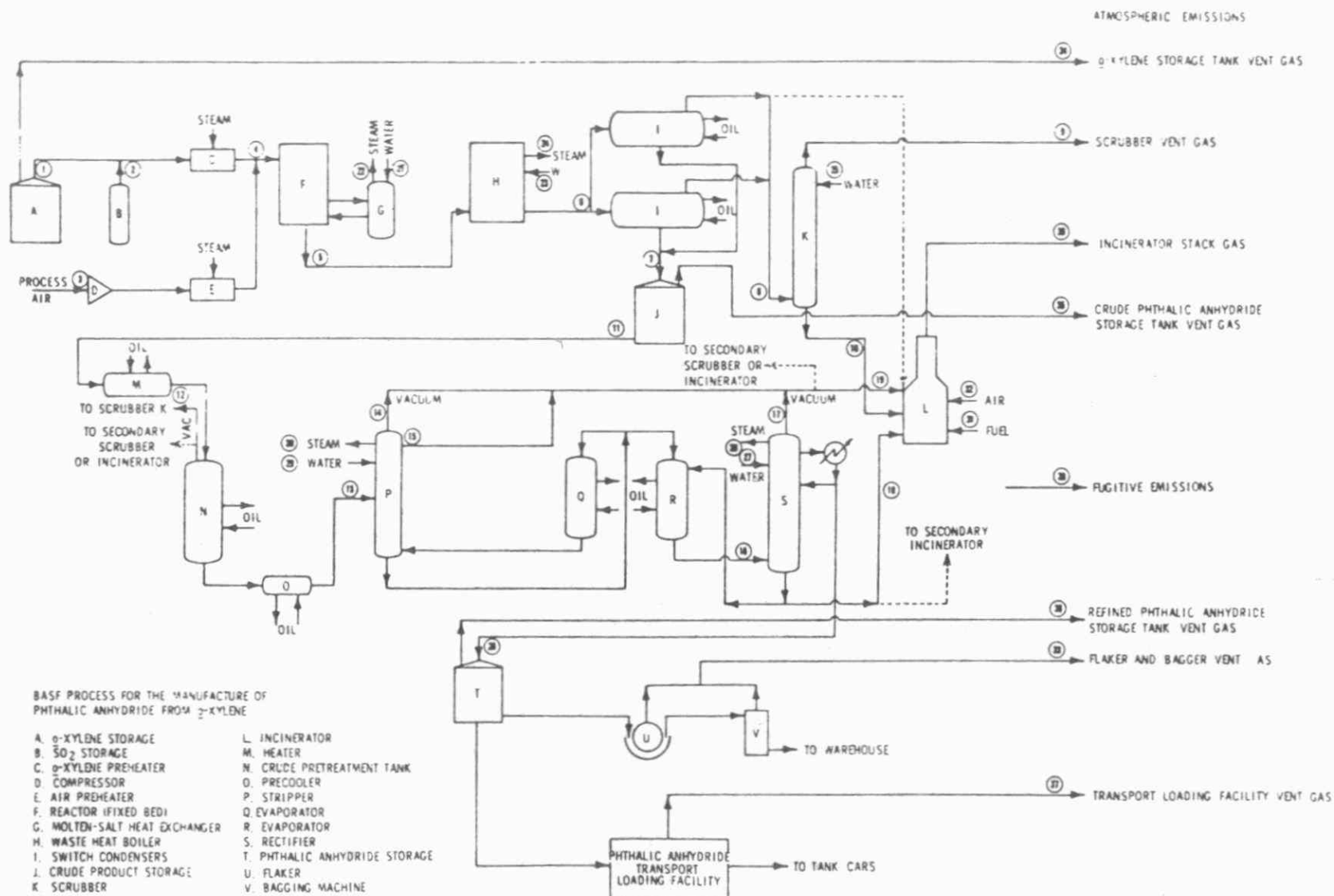


FIGURE 9-8

BASF PROCESS FOR MANUFACTURE OF PHTHALIC ANHYDRIDE FROM O-XYLENE

TABLE 9-6

STREAM CODE FOR BASF PROCESS ILLUSTRATED IN FIGURE 9-8

<u>STREAM</u>	<u>IDENTIFICATION</u>	<u>STREAM</u>	<u>IDENTIFICATION</u>
1	o-Xylene feed	20	Refined phthalic anhydride
2	Sulfur dioxide	21	Water to steam generator
3	Filtered air	22	Generated steam
4	Reactor feed	23	Water to waste-heat boiler
5	Reactor product	24	Steam from waste-heat boiler
6	Boiler effluent	25	Scrubber makeup
7	Crude product	26	Incinerator stack gas
8	Condenser off-gas	27	Water to cooling coil
9	Scrubber vent	28	Steam from cooling coil
10	Scrubber liquid purge	29	Water to cooling coil
11	Crude phthalic anhydride product	30	Steam from cooling coil
12	Pretreatment exhaust	31	Incinerator fuel
13	Pretreated crude	32	Combustion air
14	Stripping column exhaust	33	Flaker and bagger vent
15	Stripping column overhead	34	o-Xylene storage vent
16	Rectifying column feed	35	Crude product storage vent
17	Rectifying column vacuum exhaust	36	Refined phthalic anhydride storage vent
18	Rectifying column bottom product	37	Loading facility vent
19	Distillation light ends	38	Fugitive emissions



34.1 kg/hr SO_2
1,100 kg/hr CO
3,800 kg/hr CO_2
167.3 kg/hr phthalic anhydride
315.4 kg/hr maleic anhydride
20.4 kg/hr benzoic acid
11 kg/hr aldehyde

For a process utilizing a wet scrubber for the off-gas and an incinerator for the scrubber purge liquid, an efficiency of 96 % can be expected for organics removal.

Table 9-7 (6) presents estimated emissions factors for each emission source of an o-xylene-based phthalic anhydride plant.

Table 9-8 presents the estimated total emissions for a plant producing 45 Gg/annum of phthalic anhydride by the BASF process.



TABLE 9-7

EMISSION FACTORS FOR PHTHALIC ANHYDRIDE PLANT

o-XYLENE BASED - PRODUCTION 5.9×10^4 METRIC TONS/YR.SCRUBBER-INCINERATOR CONTROLSOURCE

COMPONENT	SCRUBBER VENT g/kg	INCINERATOR g/kg	STORAGE		VENTS		FLAKING & BAGGING		LOADING		CATALYST ST.		FUGITIVE g/kg
			U g/kg	C g/kg	U g/kg	C g/kg	U g/kg	C g/kg	U g/kg	C g/kg	U g/kg	C g/kg	
Phthalic anhydride	0.44	-a-	.39	.004	0.1	.001	0.45	.005					
Maleic Anhydride	1.13	-a-											
Benzoic Acid	0.94	0.50											
Carbon Monoxide	150.7	2.50											
Carbon Dioxide	520.4	379											
Nitrogen Oxides		0.19											
Sulfur Oxides	4.69												
O-Xylene			0.19	.002									
Particulate	0.63	0.44									.41	0.01	
Diphenyl Oxide													.016
Combined Hydrocarbons													0.10

Notes:

-a- Not available
 U Uncontrolled Emissions
 C Controlled Emissions





TABLE 9-8

ESTIMATED EMISSIONS FOR A 45 Gg/YR¹ PHTHALIC ANHYDRIDE PLANTSCRUBBER-INCINERATOR CONTROL

COMPONENT	SOURCE (MT/YR)										FUGITIVE
	SCRUBBER VENT	INCINERATOR	STORAGE VENTS		FLAKER & BAGGING		LOADING		CATALYST ST.		
			U	C	U	C	U	C	U	C	
Phthalic Anhydride	20		20	.18	4.5	.04	20	0.22			
Maleic Anhydride	50										
Benzoic Acid	40	20									
Carbon Monoxide	6,800	110									
Carbon Dioxide	23,400	17,060									
Nitrogen Oxides		10									
Sulfur Oxides	200										
o-Xylene			10	.09							
Particulate	30	20							18.4	0.45	
Diphenyl Oxide											0.72
Combined Hydrocarbons											4.5

¹ Estimated capacity of B.A.S.F. Ltd. facility in Cornwall, Ontario.

9.7 COKING

9.7.1 INTRODUCTION

Metallurgical coke is manufactured to provide a suitable reducing agent for blast furnace operation in the steel making industry. In Ontario, coke manufacturing facilities are located at the three major integrated steel plants.

9.7.2 MANUFACTURE OF COKE

9.7.2.1 FEEDSTOCK

Coking operations in Ontario use a bituminous coal obtained primarily from West Virginia, U.S.A. The coal feed is crushed, and screened to obtain the desired size fraction. Coals of varying volatility are stored separately and blended before charging, to obtain the desired mixture.

9.7.2.2 PROCESS DESCRIPTION

The coke manufacturing process involves the use of slot-type ovens which are grouped together to form a battery. Coal is fed or "charged" from a larry car through ports located on top of the oven. Four meter ovens hold approximately 16.5 tons of coal and five meter ovens hold approximately 27 tons of coal.

Heat is supplied indirectly from a gas-fired regenerative combustion system located below the oven, with flues between the ovens. The coking period is approximately 17 hours with coke temperatures reaching 1100 °C. At the end of a cycle, when coking is complete, the doors on both sides



of the oven are removed and the coke pushed out of the oven into an open railway car using a ram. The coke is then transported to a quench tower where water is sprayed for cooling and the coke transferred for use in the blast furnace.

During carbonization, about 20 to 35 percent by weight of the initial coal charge is evolved as mixed gases and vapors. The gases and vapors leave the oven through an ascension pipe at the top of the oven and enter the collecting main. Leakage from the oven is reduced by maintaining the oven and collecting main under negative pressure.

In the ascension pipe and the collecting main the gases are cooled by spraying with a weak ammonium liquor. As the gas cools, the tar and ammonia liquor are condensed. The liquor/tar mixture enters a decanter where they are separated. The non-condensed gas enters a light oil recovery system.

In the light oil recovery system, the gas is scrubbed with a petroleum wash oil to remove the light oils from the gas. The light oils are removed from the wash oil by heating the mixture to 100 to 140 °C and then distilling with direct steam. The mixture of light oil and steam passes out of the top of the still through separators which remove the water. The light oil then passes through a condenser and finally to storage.

In Ontario, both the light oils and the coal tar are shipped to outside firms for further treatment.



9.7.2.3 EMISSIONS/DISCHARGES

The primary points of emission during the coking process are:

- charging ports and levelling bars during charging
- leaks during carbonization at charging ports and oven doors
- oven doors during pushing
- quench tower

The primary points of discharge during the coking process are:

- quench water (approximately 335 litres per metric ton of coke)
- pitch sludge from the tar decanter
- two of the steel plants use wet electrostatic precipitators to collect emissions from the coke oven batteries. Slurries from the precipitator are a source of discharge.

During the charging some of the hydrocarbons such as anthracene, phenanthrene, and naphthalene, are volatilized, and escape. Some of the coal also breaks down to yield methane and light aromatics such as benzene.

The smoke evolved during the coking cycle contains polycyclic aromatic hydrocarbons.

Emissions created during the pushing sequence are dependent on the degree of coking. Well coked coal will smoke very little, while poorly coked "green" coke will cause excessive emissions.

Emissions from quenching can be reduced by the installation of baffles near the top of the stack.



Table 9-9 (7) presents emission factors which could be expected from a by-product coking operation without controls.

Table 9-10 indicates the potential total emissions from Ontario metallurgical coke manufacturers.

Table 9-11 (8) gives an average analysis of quench water samples.



TABLE 9-9

EMISSION FACTORS FOR METALLURGICAL COKE

MANUFACTURE WITHOUT CONTROLS¹

TYPE OF OPERATION	PARTICULATES kg/MT	SULFUR DIOXIDE kg/MT	CARBON MONOXIDE kg/MT	HYDROCARBONS ² kg/MT	NITROGEN OXIDES (NO ₂) kg/MT ²	AMMONIA kg/MT
By-produce coking						
Unloading	0.2	----	----	----	----	----
Charging	0.75	0.01	0.3	1.25	0.015	0.01
Coking cycle	0.05	----	0.3	0.75	0.005	0.03
Discharging	0.3	----	0.035	0.1	----	0.05
Quenching	0.45	----	----	----	----	----
Underfiring ³	----	2	----	----	----	----

¹ Emission factors expressed as units per unit weight of coal charged.

² Expressed as methane.

³ The sulfur dioxide factor is based on the following representative conditions: (i) sulfur content of coal charged to oven is 0.8 percent by weight; (ii) about 33 percent by weight of total sulfur in the coal charged to oven is transferred to the coke-oven gas; (iii) about 40 percent of coke-oven gas is burned during the underfiring operation and the remainder is used in other parts of the steel operation where the rest of the sulfur dioxide is discharged - about 6 lb/ton (3 kg/MT) of coal charged; and (iv) gas used in underfiring has not been desulfurized.





TABLE 9-10

POTENTIAL TOTAL EMISSIONS FROM ONTARIO
METALLURGICAL COKE MANUFACTURERS¹

TOTAL ESTIMATED CAPACITY
 6586 Gg/annum^{1,2}

MT/annum

<u>TYPE OF OPERATION</u>	<u>PARTICULATES</u>	<u>SULFUR DIOXIDE</u>	<u>CARBON MONOXIDE</u>	<u>HYDROCARBONS</u>	<u>NITROGEN OXIDES</u>	<u>AMMONIA</u>
By-product coking						
Unloading	1317	----	----	----	--	----
Charging	4940	66	1976	8232	99	66
Coking cycle	329	----	1976	4940	33	198
Discharging	1976	----	230	659	--	329
Quenching	2964	----	----	----	--	----
Underfiring	----	13,170	----	----	--	----

¹ Choquette, P.J., "Air Pollution Emissions and Control Technology: Metallurgical Coke Manufacturing Industry",
 EPS Report No. 3-AP-74-6, Air Pollution Control Directorate, Environment Canada,
 November 1974.

² Estimated percentage by company: Stelco 46.6 % - Dofasco 24.6 % - Algoma 28.8 %.

TABLE 9-11AVERAGE ANALYSIS OF QUENCH WATER SAMPLES

<u>CONTAMINANTS</u>	<u>CONCENTRATION, ppm</u>
Phenols	776
Sulfates	1066
Chlorides	1954
Total ammonia	2517
Cyanides	98
Total solids	5214



9.8 COAL TAR DISTILLATION

9.8.1 INTRODUCTION

Coal tar distillation in Ontario is conducted at two plants. One is located in Hamilton, the other in Sault Ste. Marie. Both plants are owned by Domtar Chemical Ltd.

9.8.2 COAL TAR DISTILLATION PROCESS

9.8.2.1 FEEDSTOCK

The feed is coal tar, obtained from the steel companies as a by-product of their coking process. The major compounds in the tar are: pyridine, tar acids, naphthalene, creosote and coal tar pitch.

9.8.2.2 PROCESS DESCRIPTION

The plant in Hamilton uses two fractionating columns in parallel to separate the tar into the following components: Naphthalene, wash oil, creosote, and pitch. The Sault Ste. Marie plant utilizes a pot still and obtains only one separation.

At the Hamilton operation, the tar is heated and pumped to a dehydration column where live steam is used to remove the light oils. The light oils are condensed, and separated from the water in a decanter. The bottom fraction of the dehydration column is pumped to a fractionating column when the following components are separated: tar acid oil; naphthalene; wash oil; creosote oil and pitch.

The pitch is either shipped in bulk or cooled on a steel belt and broken up to form flaked pitch.



9.8.2.3 EMISSIONS/DISCHARGES

The major points of emission are:

- fumes from blending tank (mostly naphthalene)
- pitch storage tank
- pitch loading
- pitch flaking area

The major point of discharge is the water from the light oil decanter, which is treated in a bio-oxidation system.



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10 EMISSION AND DISCHARGE
 CONTROL TECHNOLOGY



	SECTION	PAGE NO.
10	EMISSION AND DISCHARGE CONTROL TECHNOLOGY	10-1
10.1	SUMMARY	10-3
10.2	AIR EMISSION CONTROL	10-8
10.2.1	Stationary Sources	10-8
10.2.1.1	Condensation	10-8
10.2.1.2	Absorption	10-12
10.2.1.3	Adsorption	10-14
10.2.1.4	Incineration	10-30
10.2.2	Storage Tanks	10-37
10.2.3	Fugitive Sources	10-41
10.3	WASTE WATER EFFLUENT CONTROL	10-44
10.3.1	Solubility of Organic Compounds in Water	10-45
10.3.2	Toxicity to Fish	10-45
10.3.3	Free Oil Removal	10-48
10.3.4	Soluble Oil Removal	10-58
10.3.4.1	High Concentration Effluents	10-61
10.3.4.2	Low Concentration Effluents	10-66
10.3.4.2.1	Biological Oxidation	10-66
10.3.4.2.2	Activated Carbon Adsorption	10-70
10.3.4.2.3	Other Treatment Methods	10-86
10.4	WASTE DISPOSAL METHODS	10-90
10.4.1	Incineration	10-90
10.4.2	Other Methods	10-95
10.5	REFERENCES	10-97



10.1 SUMMARY

Air Emission Control

Air emission control systems are usually an integral part of manufacturing technology. As a consequence, process data are considered proprietary, and are usually not published. Thus very little information can be found in literature.

Condensation, absorption, adsorption and incineration are the most frequently used systems in controlling emissions from stationary sources.

If a multistage condensation system with refrigeration in the final stage is used, an overall removal efficiency of 99+ % can be achieved for most of the hydrocarbons of interest here.

Water, mineral oils, non-volatile hydrocarbon oils and various aqueous solutions are used for the absorption of hydrocarbons, which are usually contained in large volume gaseous streams. Absorption systems can be designed to achieve up to 90 to 95 % removal efficiency.

Adsorption on the surface of specially prepared granular solids, and adsorbents, is a very efficient method for the selective removal of hydrocarbons from gaseous streams. Activated carbon is the most widely used adsorbent. Practical sorption capacities for activated carbon vary from 6 weight % for benzene to 20 weight % for perchloroethylene.

Recently, Dow Chemical has developed a new copolymer adsorbent



which is suitable for the control of emissions of benzene, styrene, toluene, methylene chloride, allyl chloride and a number of other compounds. Insufficient experimental data exist to design an adsorption system of optimum efficiency. The development of new high capacity sorbents should be encouraged.

Incineration is a frequently used method of emission control in the petrochemical industry. 1000 °C and 2 seconds of retention time is considered satisfactory for the destruction of most organic compounds, if adequate mixing is assured by proper design. An inadequate supply of waste gases creates problems in operating an incinerator and if the off-gases are not corrosive, some form of heat recovery is desirable. An overall thermal efficiency of 60 to 80 % may be achieved.

A catalytic oxidation system reduces heat requirements by lowering the oxidation temperature. Deactivation of the catalyst and often an inadequate incineration efficiency are the main problems associated with catalytic oxidation.

Flares are not considered as environmentally satisfactory for the disposal of hazardous gases, because of incomplete combustion and noise pollution problems.

In a modern petrochemical plant, hydrocarbons are stored in a totally enclosed storage vessel. Up to 85 % reduction of emissions may be achieved by installation of a floating roof in preference to a fixed roof vessel. However, recovery units based on the adsorption principle may quantitatively eliminate emissions from fixed roof tanks.



It is estimated that 60 to 80 % of all storage facilities in Canada utilize floating roofs or their equivalents to reduce hydrocarbon losses.

Fugitive sources are one of the largest categories of hydrocarbon emissions. They include: pump seals, relief valves, pipeline valves, sampling and blind changing. There are two major studies underway in the U.S.A. to determine fugitive hydrocarbon emissions.

Waste Water Effluent Control

Large amounts of nonsolubilized aromatic hydrocarbons and other oils can be removed by:

- gravity oil-water separation to produce an effluent containing down to 50 ppm oil
- induced air flotation (IAF), dissolved air flotation (DAF) or filtration to produce an effluent containing 10-20 ppm oil
- biological oxidation or activated carbon adsorption to produce an effluent containing <10 ppm.

Soluble aromatic hydrocarbons may be removed from waste water effluents by biological oxidation. However, for many aromatics the process is slow and other methods may have to be applied.

Activated carbon is normally used as a final polishing step for complete contaminant removal. Nonpolar hydrocarbons of molecular weight greater than 45 are adsorbable on carbon. The feasibility of activated carbon adsorption should be determined by both carbon



adsorption isotherms and continuous flow pilot plant simulation tests. Polymeric adsorbents are being developed and offer better sorption properties for specific compounds.

A complete removal of hydrocarbons from waste water effluents can be achieved by:

- primary treatment such as gravity oil-water separation and IAF, DAF or filtration followed by
- the series: biological oxidation - carbon adsorption treatment or
- the series: carbon adsorption - biological oxidation treatment or
- carbon adsorption as the only treatment

Other available technologies are steam stripping, solvent extraction, membrane processes and wet air oxidation.

Waste Disposal Methods

Incineration is an ultimate disposal method if properly designed and operated. 1000 °C and 2 seconds residence time is considered adequate for the thermal destruction of most organic compounds. Incomplete combustion of chlorinated hydrocarbons may result in emissions of phosgene and chlorine. Excess hydrogen is required to form hydrogen chloride, which may be neutralized or recovered in the form of 15-20 % acid. When extractive distillation is used, higher grade acid may be produced. No more than 10 ppm of chlorine and hydrogen chloride have been reported in the hydrogen chloride recovery plant tail gas.



Cement kiln incineration is a safe disposal method for organic compounds, particularly for chlorinated materials, where the formation of chloride ion has been found to improve the quality of the cement produced.

Deep wells and land fills have often been used in the past to dispose of chemical wastes. However, it has become more and more difficult to find sites for disposal where there is no risk of ground water contamination.

With the latest processing technology, the production of waste in petrochemical plants is significantly minimized.



10.2 AIR EMISSION CONTROL

Little information is available on the usage of air pollution control systems in hydrocarbon-producing and -consuming industries. The aromatic hydrocarbons of interest here are usually produced by integrated petrochemical plants, where they are also used as intermediates, as discussed in Section 8. Processes producing and/or using aromatic hydrocarbons have recovery systems as an integrated part of their technology.

The most frequently used systems are condensation, absorption, adsorption and incineration.

10.2.1 STATIONARY SOURCES

10.2.1.1 CONDENSATION

Condensers have found a wide range of applications in the organic chemical industry, where their purpose has been to condense concentrated vapors in the primary process. Control of organic emissions by condensation is limited by the equilibrium partial pressure of the component. As condensation occurs, the partial pressure of the compound remaining in the gas phase decreases rapidly and complete condensation is not possible. For example, even at 0 °C, toluene has a vapor pressure of about 0.8 kPa; at atmospheric pressure (101.3 kPa), a gas stream saturated with toluene still contains about 8,000 ppm of that gas. For this reason, condensers are usually followed by a secondary system such as an adsorber, absorber or incinerator.

Condensation is mostly utilized to remove a relatively high hydro-



carbon concentration from small noncondensable waste gas flows. The main advantage of condensation is that the product may be recovered at relatively low energy requirements and cost (1). Hydrocarbon removal efficiency depends on:

- composition of the waste stream
- operating temperature
- condenser design

and may vary between 40 and 99.9 %.

Since condensation is usually accomplished by decreasing the temperature of the vapor, a cold surface or a cooling liquid is deployed in the gas stream to induce condensation. Condensers may be classified into two groups: surface and contact.

Surface Condensers include the common shell-and-tube type heat exchanger in which the cooling medium, usually water, flows through the tubes, and vapor condenses on the outside surface. The condensed vapor forms a film on the cool tubes and drains to storage for further recovery of valuable compounds or incineration. Cooled condensers are usually designed with finned tubes, and the vapor condenses outside the tubes.

A series of two, three or more heat exchangers (condensers) may be used to improve the removal efficiency. Different cooling media may also be used in individual stages as shown in Figure 10-1. A very low temperature in the third stage with refrigeration is needed for an overall removal efficiency of 99+ % (2, 13). This may cause operational problems if water vapor is present (Figure 10-1).

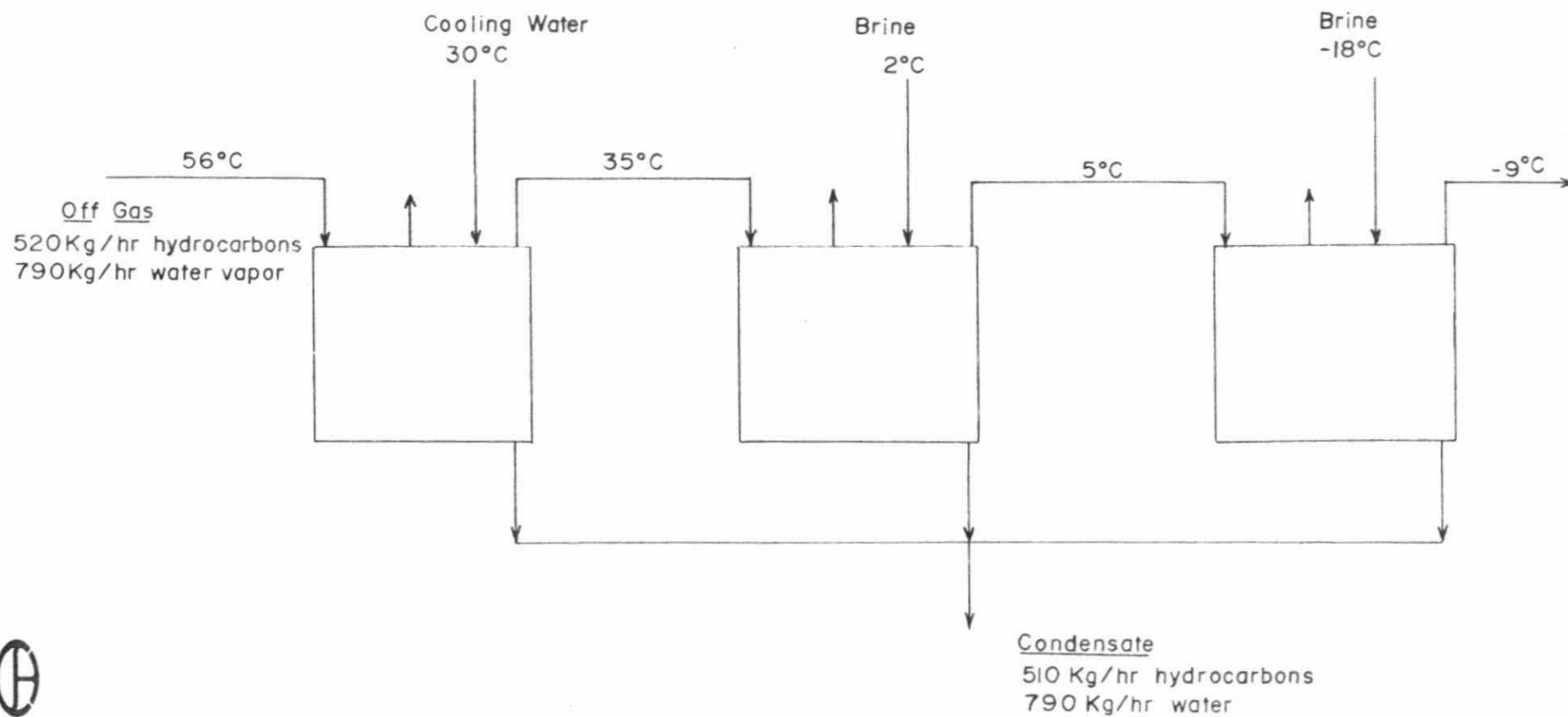


FIGURE 10-1

HYDROCARBON CONTROL SYSTEM - CONDENSATION

Surface condensers are used, for example, in styrene production processes to control benzene emissions from distillation columns. It is reported (6) that the benzene emissions were reduced to 4.0×10^{-3} kg/kg styrene produced.

Contact Condensers cool the vapor by spraying a cold liquid directly into the gas stream. The condensed vapor and cooling liquid mixture is then treated in a recovery unit or effluent control plant. Contact condensers are, in general, less expensive, more flexible, and more efficient in removing organic compounds, than surface condensers. However, the cost of recovering hydrocarbons from the cooling medium may not improve the overall economics of a contact condensation system. J.R. Fair (12) outlines the design procedures for an optional contact condenser system.

Both contact and surface condensers can be easily applied to elevated pressure technology. Elevated pressure proportionately increases the vapor pressure of condensable hydrocarbons. This results in better removal efficiency (6, 44). For example: a condenser treating the oxidizer vent from a cumene manufacturing process operates at 506 kPa and reduces the benzene emissions to 10^{-5} kg/kg of cumene produced. Condensers have been used successfully, either separately or with additional controls, in a number of processes such as (14, 19): alkylation unit accumulator vents, styrene processing units, toluene recovery accumulation vents, UDEX extraction units and solvent recovery systems.

Unfortunately, no detailed operating data are available in the literature as these data are considered to be an integral part of



proprietary technology.

Fog formation is a potentially serious yield loss and pollution problem for all processes that involve partial condensation. D.E. Steinmeyer (15) presents a number of examples of fog formation in the cooling systems of streams containing benzene, carbon tetrachloride, trichloromethane and chlorobenzene. In order to minimize fog formation it is suggested (15):

- to use lower temperature differences in the condenser
- to obtain uniform cooling

10.2.1.2 ABSORPTION

Absorption of hydrocarbons in the petrochemical industry is an important manufacturing step. As with condensation, absorption is considered a preliminary step in air pollution control because it does not remove enough of the hydrocarbons to provide a complete control. This technique is used commonly, and is often found to be profitable in petroleum and petrochemical operations for gaseous streams with a relatively high concentration of hydrocarbons.

Common absorbents for organic vapors are water, mineral oil, non-volatile hydrocarbon oils and various aqueous solutions (2-5)

In the absorption process, a soluble component of a gas mixture is dissolved in a relatively non-volatile liquid. Condensation operations may precede this absorption process (1, 6, 7). The ideal absorbent should meet most of the following requirements (8):

- the gas (to be absorbed) should be quite soluble in the



absorbent to enhance the rate of absorption and to decrease the quantity of absorbent required

- the absorbent should be relatively non-volatile to prevent losses and contamination of the gaseous stream
- the absorbent should be non-corrosive to reduce maintenance costs
- the absorbent should have a low viscosity to increase absorption and reduce flooding (packed towers)
- the absorbent should be low in toxicity, non-flammable, chemically stable and have a low freezing point

Creosote oil or gas oil is commonly used for the absorption of benzene, toluene and xylenes (9). A common practice is the use of tower scrubbers in which the gas and wash oil flow counter-currently. The factors which influence the absorption system performance are:

- temperature
- gas/oil ratio
- quality of oil

Operating temperatures should be as low as practicable in order to reduce hydrocarbon vapor pressure in the oil. The gas/oil ratio may vary from 1 to 5 m³ of oil per 100 m³ of gas depending on the type of tower, the concentration of hydrocarbons in the inlet stream, the outlet concentration, and the physicochemical properties of the wash oil. The "drop point" of the wash oil should be about 200 °C and the boiling point between 200 and 300 °C. Creosote oil has a higher sorption capacity than gas oil (4 % vs 3 % by weight). Viscosity is the most



important property of wash oils for use in this application and should be between 30 and 35 sec Redwood at 20 °C.

It is reported that an absorption system is capable of reducing the emissions of a benzene-toluene mixture from a styrene recovery plant to $3 \text{ to } 4 \times 10^{-3}$ kg/kg of styrene and about 3×10^{-3} kg of ethylbenzene/kg of styrene. A 90 to 95 % absorption efficiency of benzene has been reported (10).

A detailed description of absorption towers and design procedures has been published (8, 9).

10.2.1.3 ADSORPTION

Adsorption processes for gas purification are based on the physical properties of specially prepared granular solids, known as adsorbents, which selectively attract and retain gases on their surfaces (11, 16, 21, 22). The most widely used adsorbents are activated alumina, activated carbon, silica gel and molecular sieves. An adsorption process operates on a cyclical basis. The gas and adsorbent are contacted until the desired point of saturation is reached; the adsorbent is then removed from the gas stream and desorbed.

All adsorption processes are exothermic. The heat of adsorption due to surface attraction is greater than the heat of condensation of the gases being adsorbed.

Adsorption increases progressively with increase in the partial pressure of the gas. At low partial pressure, adsorption is by surface attraction, and at higher partial pressures the smallest wetted



capillaries become effective and condensation begins. At higher pressures the larger capillaries become effective (Figure 10-2 shows the relationship between maximum effective pore size and vapor pressure (or vapor concentration) for benzene at 20 °C as computed on the basis of the capillary condensation theory (9)). The relationship between pressure and amount adsorbed depends upon:

- the pore size distribution of the adsorbent
- the exposed surface area
- the nature of the sorbent and gas

This relationship is expressed graphically in the form of adsorption isotherms and must be determined experimentally. The adsorption isotherms are expressions of the amount of gas adsorbed under true static equilibrium conditions (Figure 10-3, 10-4).

Very little quantitative data are available on the adsorption of a mixture of gases and vapors. A preferentially adsorbed gas will displace other gases which have already been adsorbed.

The application of adsorption in air pollution control involves the use of a dynamic system (20, 21). The adsorbent is generally used in a fixed bed and the contaminated air or gas is passed through it. Depending on the amount collected and its market value, the contaminant is either recovered or discarded when saturation of the adsorbent necessitates regeneration. Although isotherms (for static conditions) are indicative of the efficiency of an adsorbent, they do not supply data to enable the calculation of contact time or the amount of adsorbent required to reduce the contaminant concentration below the



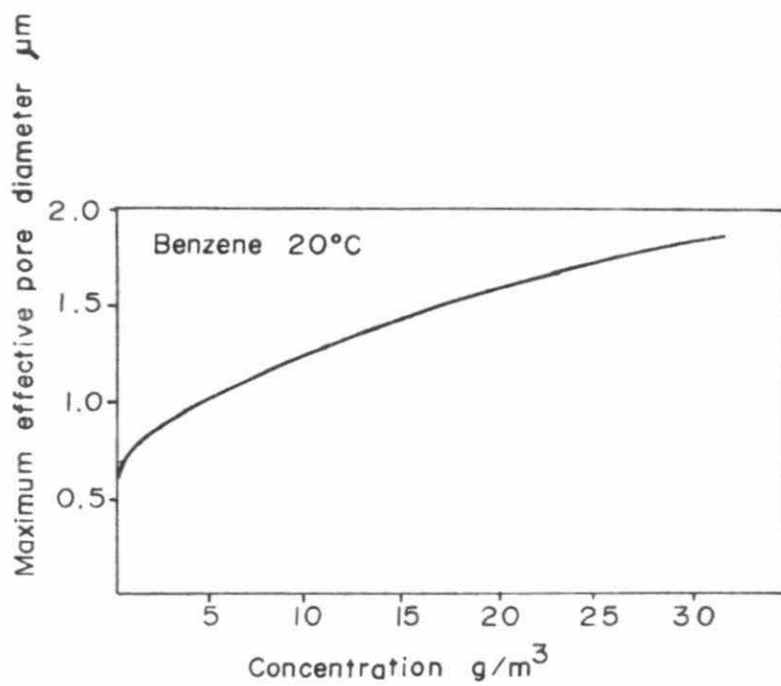


FIGURE 10-2

RELATIONSHIP BETWEEN PORE SIZE AND
VAPOR CONCENTRATION



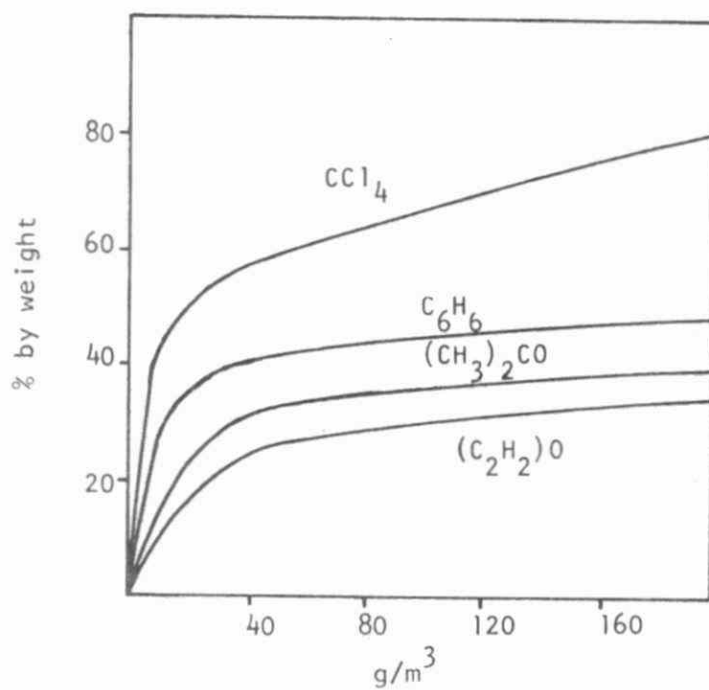


FIGURE 10-3

ADSORPTION ISOTHERMS FOR SOLVENTS ON ACTIVATED CARBON



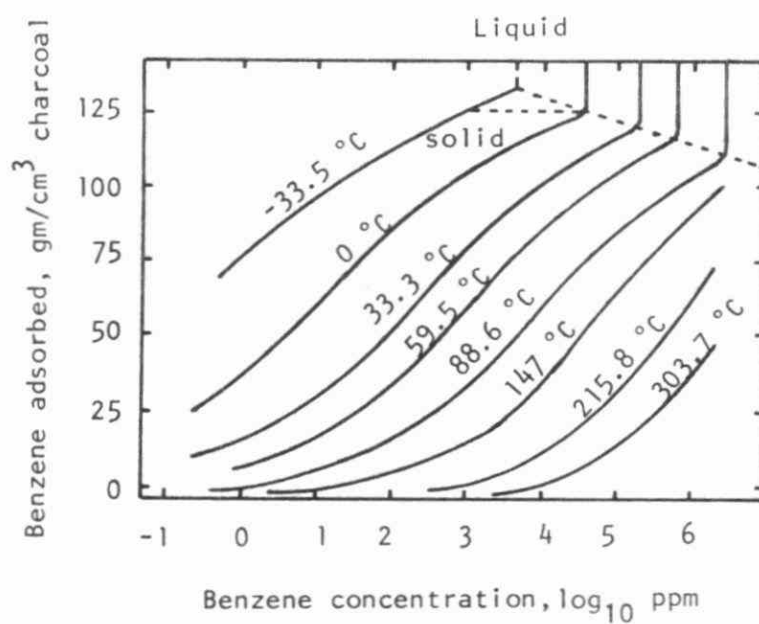


FIGURE 10-4

ADSORPTION ISOTHERMS OF BENZENE ON ACTIVATED COCONUT CHARCOAL
AT ATMOSPHERIC PRESSURE (3)



desired limits.

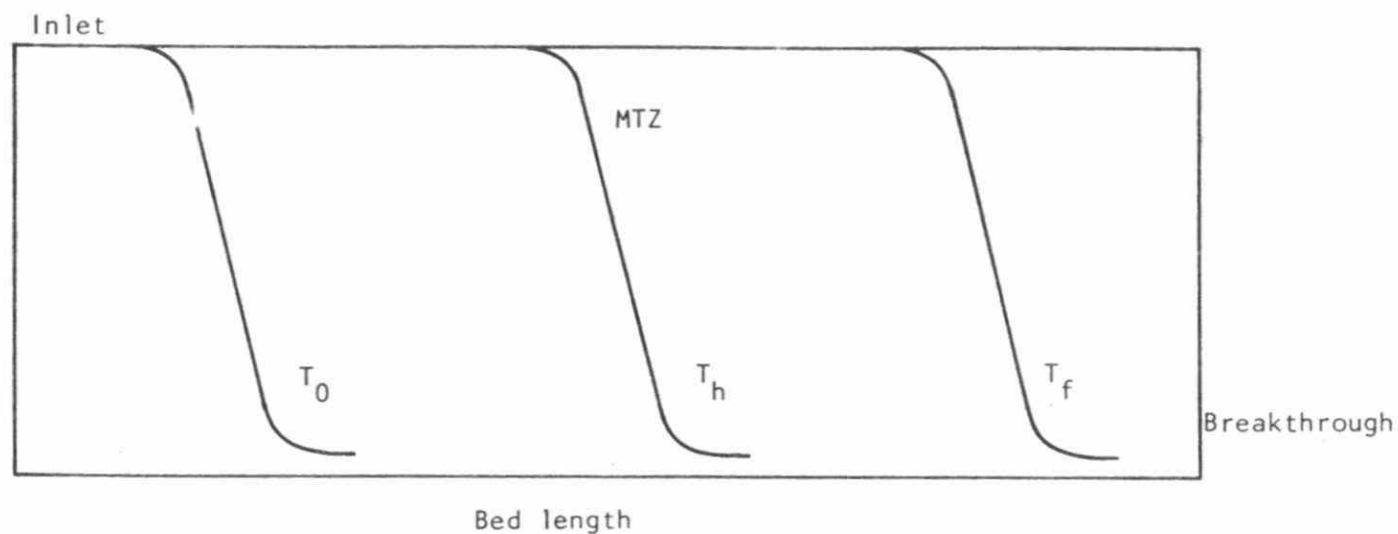
When a gas is first passed through a bed of adsorbent, most of the contaminants are initially adsorbed at the inlet part of the bed.

Later, when the adsorbent at the inlet end becomes saturated, adsorption takes place further along the bed.

The situation in the bed while it is in normal operation may be represented by Figure 10-5. That portion of the bed in which the adsorbate concentration transition occurs is defined as the mass-transfer-zone (MTZ) (16). As more gas is passed through, the saturated zone moves forward until the breakthrough point is reached, at which time the exit concentration begins to rise rapidly above whatever limit has been fixed as a desirable maximum. While the concentration at saturation is a function of the adsorbent material used and the operating temperature, the dynamic capacity is also dependent on other operating conditions such as inlet concentration, gas flow and bed depth. It is extremely important that the adsorber bed should be at least as long as the transfer zone length of the key compound to be adsorbed. Therefore, it is important to know the depth of this mass transfer zone. The following factors play the most important role in dynamic adsorption and the length and shape of the MTZ:

- i) the type of adsorbent
- ii) the particle size of an adsorbent
- iii) the depth of the adsorbent bed
- iv) the gas velocity
- v) the temperature of the gas stream and the adsorbent





T_0 = MTZ concentration gradient at the formation of the zone
 T_h = MTZ concentration gradient at half life
 T_f = MTZ concentration gradient at breakthrough

FIGURE 10-5
 FORMATION AND MOVEMENT OF THE MTZ THROUGH AN ABSORBENT BED



- vi) the concentrations of the contaminants to be removed
- vii) the concentrations of the compounds not to be removed, including moisture
- viii) the pressure of the system
- ix) removal efficiency
- x) possible decomposition or polymerization of contaminants on the adsorbent

i) Selection of Adsorbent

The preferential adsorption characteristics and physical properties of the industrial adsorbents determine their main applications. All of the adsorbents are capable of adsorbing organic solvents, impurities and water vapor from the gas stream, but each has a particular affinity for water vapor or organic vapors. Activated carbon is the most commonly used for organic vapors. The main advantage is its ability to recover organic solvents present at low concentrations in the gas stream. For satisfactory adsorption, the molecular weight of a substance should be greater than 45; benzene and the other hydrocarbons of interest here easily meet this requirement. The following is a partial list of compounds selectively adsorbed by activated carbon (2): benzene, carbon tetrachloride, chloroform, cumene, dichloroethane, dichloroethylene, perchloroethylene, toluene and trichloroethylene. R.R. Manzone and D.W. Oaks (17, 18) report some practical sorption capacities (% by weight for activated carbon):

Benzene	6 %
Carbon Tetrachloride	10 %



Chloroform	10 %
Perchloroethylene	20 %
Toluene	7 %
Trichloroethylene	15 %
Xylene	10 %

Yun-Chung Sun and F.R. Killat of Dow Chemical (39) have described a new co-polymer adsorbent for the control of emissions of benzene, styrene, toluene, methyl ethyl ketone, methylene chloride, allyl chloride, pentane, hexane, gasoline, etc.

ii) The Effect of Particle Size

The dimensions and shape of the adsorbent particles affect both pressure drop through the adsorber bed and the diffusion ratio into the particles. Adsorber beds consisting of smaller particles, although causing a higher pressure drop, are more efficient and will produce a smaller MTZ.

iii) The Depth of the Adsorber Bed

It is primarily important that the depth of the bed be larger than the unsaturated length of the transfer zone. Secondly, a more than proportional increase of capacity is achieved for any multiple of the minimum bed depth. The MTZ is usually determined by experiment.

iv) Gas Velocity

The velocity of the gas stream through the adsorbent bed is limited by the adsorbent crushing velocity. The length of the MTZ is directly proportional to velocity. In practice, however, volume velocity is



usually used and for most common activated carbons, a volume velocity of 1 l/sec can be treated by 50 kg of carbon (17, 18). Properly conducted pilot plant tests can significantly optimize the operating parameters.

v) Temperature

Generally, adsorption decreases with increasing temperature. The equilibrium capacity of adsorbents is lower at higher temperatures; the dynamic capacity is also lower. Figure 10-6 shows the variation of benzene vapor adsorption on carbon with temperature. Most carbon adsorbents are satisfactory for use up to 150 °C.

vi) Concentration of Contaminant

The adsorption capacity of adsorbents is directly proportional to the concentration of the contaminant. It is also inversely proportional to the length of the MTZ; for example, a deeper bed will be required to remove a lower concentration contaminant with equal efficiency than to remove the same contaminant at higher concentrations. It is very important that, for combustible gases, the concentration entering the adsorbent is kept below the lower explosive limits (17, 18):

Benzene	1.4 % (volume in air)
Toluene	1.27 %
Ortho-xylene	1.0 %
Para-xylene	1.1 %

Concentrations on the order of 25-50 % of the lower explosive limit are used in commercial practice (9).



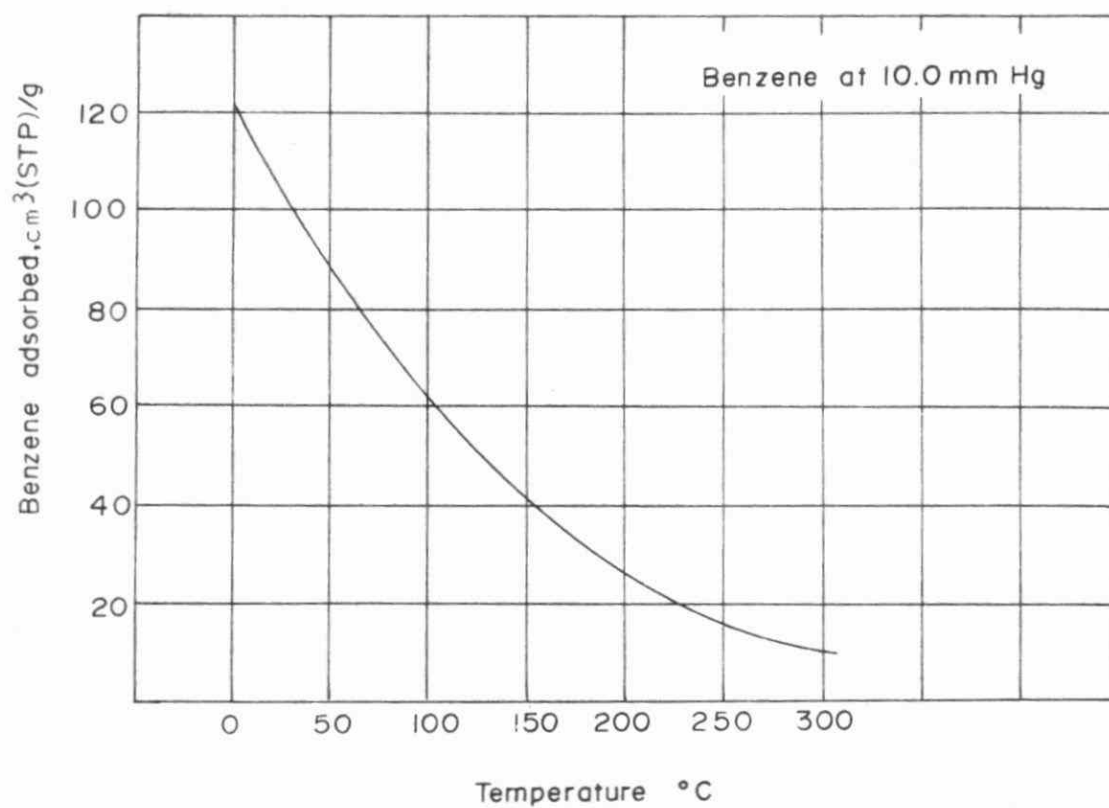


FIGURE 10-6

BENZENE ADSORPTION ISOBAR ON CARBON



In general, fixed bed adsorbers have not been used to recover organic vapors when the vapor-laden stream contains less than 2,700 ppm (2). There is a range of vapor concentration for which profitable recovery of organics cannot be obtained. This range, between a few ppm and about 1000 ppm, is often unsuitable for non-regenerative systems because of the high cost of adsorbent replacement. For such a range, instead of desorption, oxidative regeneration of the adsorbent has been suggested (2).

vii) Concentration of the Compounds not to be Removed

It is important to realize that some portion of all gases present will be adsorbed because these gases compete for the available surface area. Although activated carbon is less sensitive to moisture than other adsorbents, its adsorption capacity in the presence of water vapor can be considerably lower than adsorption from a dry gas stream. It is preferable to adsorb organics from a low relative humidity gas stream.

viii) Effect of Pressure

Generally, the adsorption capacity of the adsorbent increases with increasing pressure. However, at high pressures (over 3.5 MPa) a decrease in capacity is observed due to retrograde condensation and increased adsorption of the carrier gas.

ix) Removal Efficiency

Removal efficiency is an important design parameter and depends on the needs of the plant. Naturally, deeper adsorbent beds are required to achieve a 99.9+ % single pass removal, than for a partial 60-80 % removal efficiency.



x) Decomposition and Polymerization

Some hydrocarbons may decompose, react or polymerize when in contact with the adsorbent. The decomposed product may be adsorbed at a lower capacity than the original substance. Polymerization on the adsorbent surface will significantly lower its adsorption capacity.

Adsorption Systems

Adsorption systems may be classified as

- regenerative or
- non-regenerative

Regenerative systems are used when the adsorbent is to be reactivated by desorption and the desorbed vapors recovered for reuse or disposal (Figure 10-7).

Non-Regenerative systems are used when the adsorbent is to be replaced with fresh materials; the displaced material is sent for central regeneration or for disposal. It is usually used for small commercial applications, and will not be discussed in this report.

Regenerative Adsorption Systems

A desirable feature of using an adsorption system for the control of hydrocarbon emissions is its ability to recover the adsorbed hydrocarbon on regeneration. To remove the adsorbate, the sorbent must be heated to a temperature above that at which the hydrocarbon was adsorbed. Desorbed vapors are removed by a carrier gas, usually steam.



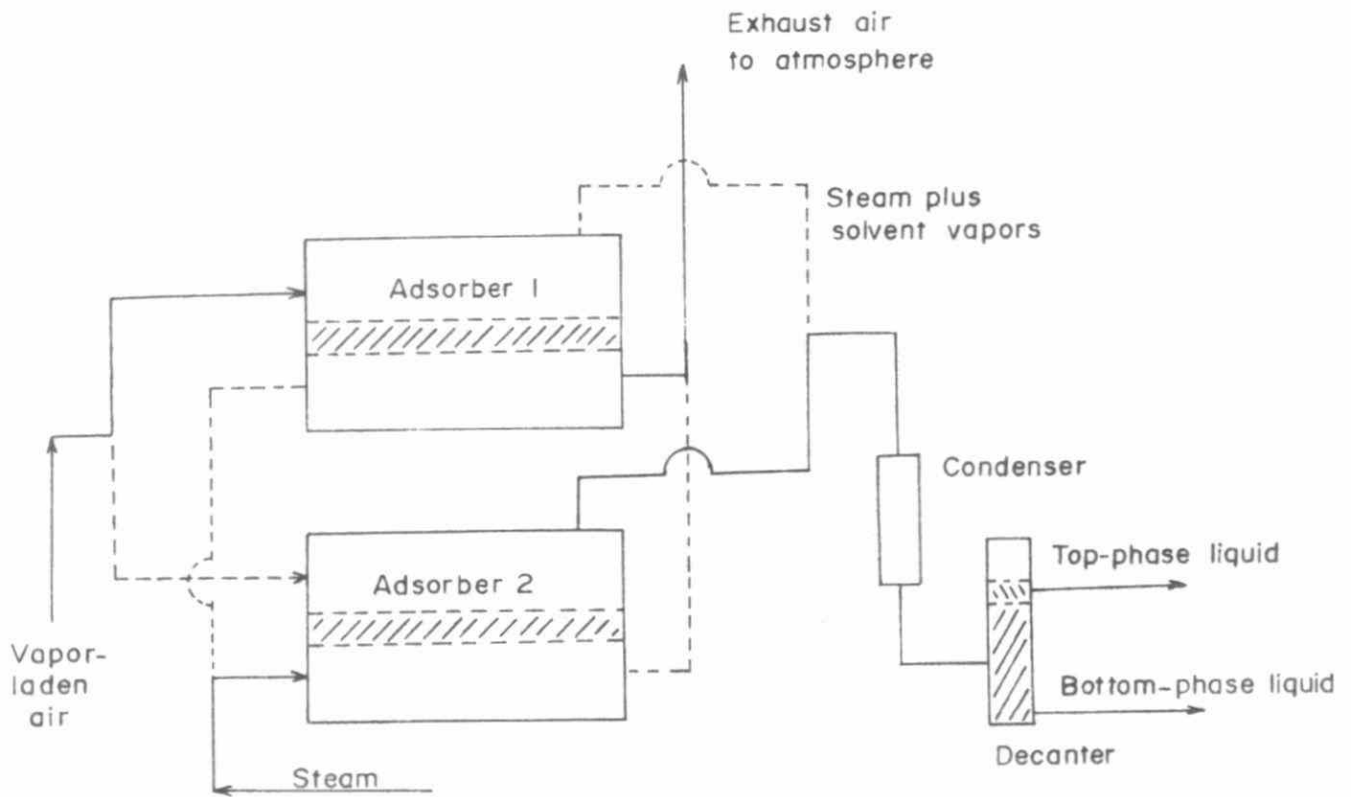


FIGURE 10-7

TWO-UNIT FIXED-BED ADSORBER (2)

The steam passes through the bed at 1/10 or 1/5 of the air velocity, heats the bed, and carries desorbed hydrocarbons from the adsorber to a condenser (Figure 10-7) where hydrocarbons and steam are condensed. The hydrocarbons are then separated from the condensed water. Hot air and a partial condenser may also be used. A well-designed plant will have a steam consumption in the range of 1 to 10 kg of steam per kg of recovered hydrocarbon (9, 19). Steam consumption for desorption of toluene and perchloroethylene is discussed in detail by J.A. Danielson (19). R.D. Fulker (11) outlines all of the factors which must be considered in designing the desorption process.

The adsorption process involves mass transfer as well as adsorption, and no adequate design and scale up procedures are available which include this consideration (2). In actual practice, the adsorption capacity, height of the bed, and stripping conditions for a given gas stream and type of hydrocarbon are obtained experimentally in pilot plant units (Figure 10-8) and the design data are considered proprietary (20).

Activated carbon sorbent beds are identified as effective emission control devices for recovering cumene. Pressure and temperature conditions for the stream entering the carbon bed are such that a relatively high cumene content is present and a recovery efficiency of between 82 and 91 % is achieved (36). W.D. Lovett and F.T. Canniff (45) report the application of carbon adsorption in combination with incineration, with fuel economy as the main objective. Air containing 85 ppm of benzene is concentrated to 3,500 ppm and incinerated. The effect of concentration is an 86:1 reduction of energy requirements.



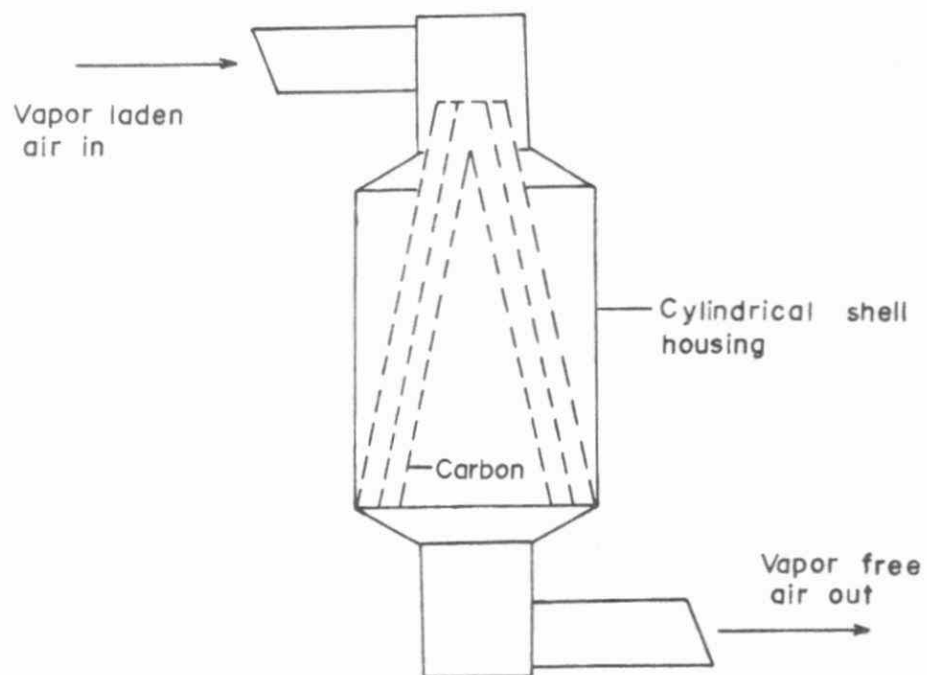


FIGURE 10-8

VERTICAL ADSORBER WITH TWO CONES
(permitting studies on different depths of carbon beds)(2)

10.2.1.4 INCINERATION

Incineration is another process for the control of gaseous, liquid or solid wastes. The objective is to oxidize as completely as possible organic materials emitted and/or discharged from a process or operation. It is essentially a straightforward combustion process in which oxygen (in air) must be mixed with the combustible at some temperature above its autoignition temperature. Typical values of autoignition temperatures for some hydrocarbons are listed below (23, 24).

	°C
Toluene	508
Styrene	490
Ethane	515
Ethylene	450
Benzene	498
Ethylbenzene	432
o-Xylene	464
m-Xylene	528
p-Xylene	529
Styrene	490
Naphthalene	526
Methyl Chloride	632
Ethyl Chloride	519
Dichloroethylene	460
Trichloroethane	486
Trichloroethylene	420



When starting with a waste in liquid form, it is necessary to supply sufficient heat for evaporation in addition to raising it to its ignition temperature.

There are a number of different types of incinerators used to oxidize gaseous materials and they can be classified into 3 categories:

- i) flares
- ii) direct flame
- iii) catalytic oxidation

i) Flares (29)

Large volumes of hydrocarbon gases are produced and handled in a modern petrochemical plant. Usually these gases are controlled within the process. Sudden or unexpected upsets and scheduled shut-downs in the process units, however, can produce gas in excess of the capacity of the hydrocarbon recovery system.

Emergencies that can cause the sudden venting of excessive amounts of gases and vapors include fires, compressor failures, over-pressures in process vessels, line breaks, leaks and power failures.

Excess gas is usually incinerated in flares. Flares are mostly elevated to safely dissipate heat and disperse any vapors that may be emitted. Smoke is a by-product of incomplete combustion. Smokeless combustion can be obtained in an elevated flare by the injection of an inert gas to the combustion zone to provide turbulence and inspire air. The most commonly used air-inspiring material is steam. However, smokeless burning of large quantities of gases by flares presents some



serious design problems. Flares are generally not environmentally satisfactory for disposal of hazardous gases because of incomplete combustion, breakdown products, and noise pollution problems.

ii) Direct Flame Incineration

Whereas flares are used for destruction of waste gases which are released at concentrations above the lower limit of flammability, gases vented from the discussed processes are generally exhausted at concentrations below the lower flammable limit (around 25 % of the lower limit). At these concentrations of gases, combustion in an enclosed chamber is necessary.

There are three important parameters which influence the proper incineration of pollutants in a dilute stream:

- temperature
- time
- turbulence

First, the supplemental fuel is burned by utilizing part of the oxygen contained in the dilute fume stream to produce high temperature combustion products, above 1200 °C. At the same time, the rest of the cold fume by-passes the flame and is mixed with the combustion products (Figure 10-9). The mixing should give a uniform temperature to all fumes flowing through the incinerator. This is done as rapidly as possible without causing flame quenching so that sufficient residence time can be provided at the required temperature for the oxidation of pollutants contained in the by-passed fume. In actual incineration



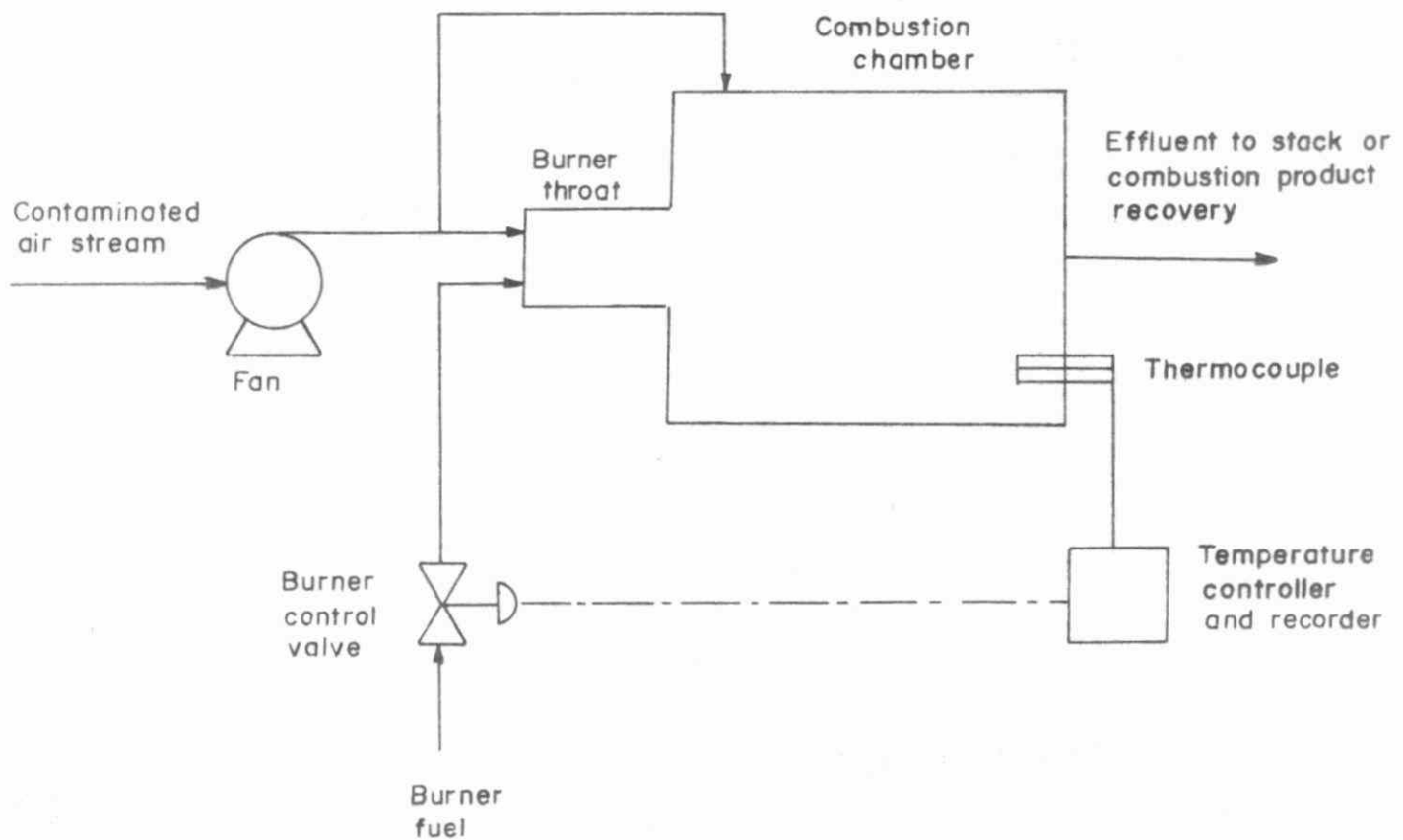


FIGURE 10-9

DIRECT-FLAME THERMAL INCINERATOR

operations, the mixing time for the gas mixture is about the same order as, or greater than, the reaction time, depending on the incinerator design. From past experience in the incineration of organic pollutants, it is reported that the destruction of most hydrocarbons occurs very rapidly at temperatures in excess of 590 °C to 700 °C. Possible exceptions are benzene derivatives, like toluene and chlorinated hydrocarbons, which are stable and require higher temperatures for complete oxidation to occur in a few tenths of a second (26). Experimental data on incineration efficiency of toluene, hexane and cyclohexane are shown in Figure 10-10. As a rule of thumb, 1000 °C and 2 seconds of retention should be satisfactory for destruction of most organic compounds including very stable chlorinated materials (25, 27).

Both the high cost and very often inadequate supply of fuel create problems in operating an incinerator. If the off-gases are not corrosive, some form of heat recovery is desirable. Two types of heat recovery equipment are usually considered:

- waste heat boiler
- feed-effluent heat exchanger

Overall thermal efficiency of 60 to 80 % may be achieved.

iii) Catalytic Oxidation

This is another method of reducing the operating costs of incineration. Contact of a waste stream with a catalyst bed allows the oxidation reaction to occur rapidly at a lower temperature than that required in a thermal direct-flame incinerator (84). Five steps are



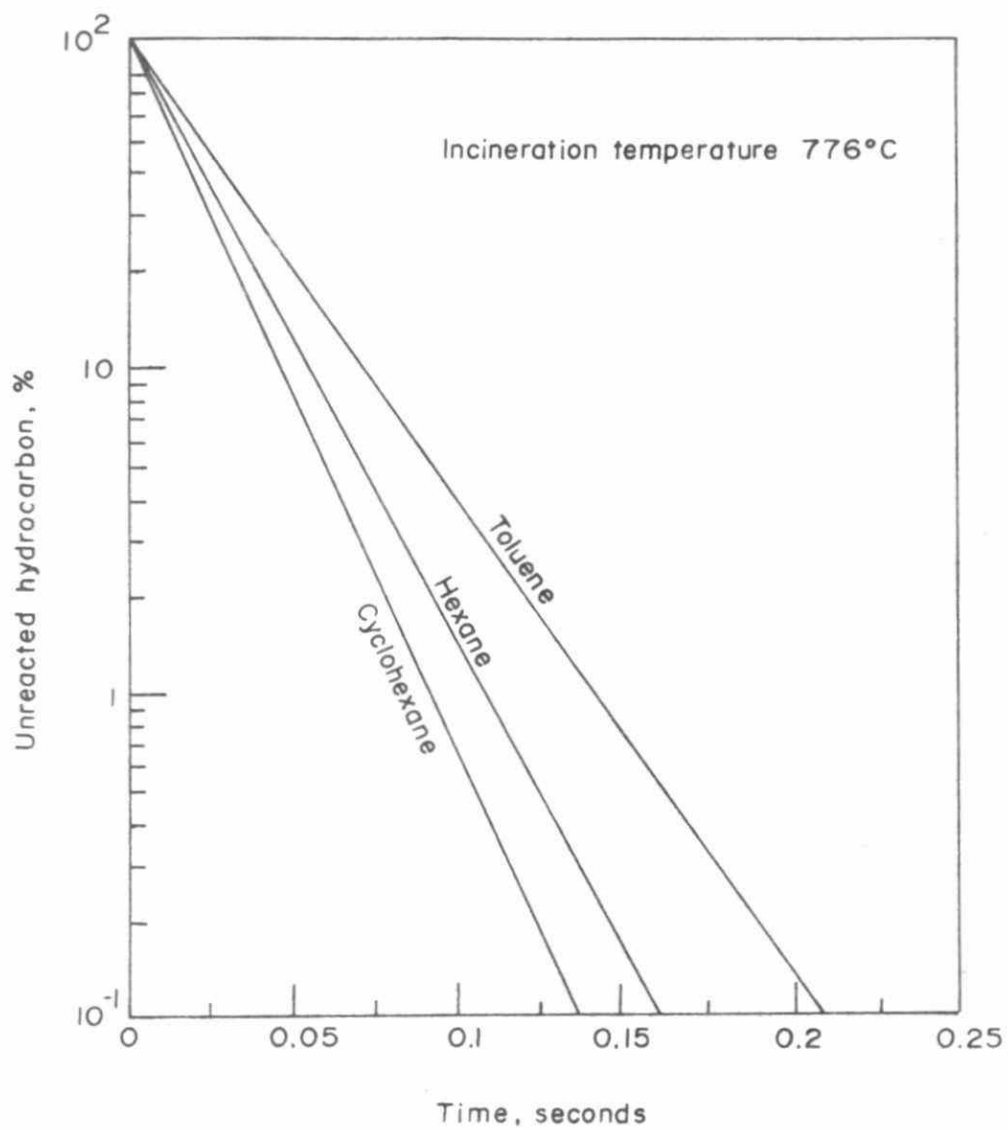


FIGURE 10-10
HYDROCARBON OXIDATION RATES IN ABSENCE OF FLAME



involved in the solid-catalyzed vapor-phase reaction:

- Diffusion of the reactants through the stagnant fluid around the surface of the catalyst
- Adsorption of the reactants on the catalyst surface
- Reaction of the adsorbed reactants to form products
- Desorption of the products from the catalytic surface
- Diffusion of the products through the surface film to the bulk vapor phase outside the catalyst

The various noble metals used as catalysts, such as platinum, palladium and rhodium, in varying concentrations, cause different reaction rates for each specific hydrocarbon. Moreover, in air pollution control, it is not practical to undertake a complex research project to develop a specific catalyst for different effluents. Therefore, commercial catalyst manufacturers have attempted to develop a universal catalyst which is effective in oxidizing a wide range of organic materials over an extended period of exposure time with minimum maintenance and replacement. Fouling and poisoning are the most frequent problems associated with the use of catalysts. One supplier (20) reports successful application of catalytic incinerators in a number of applications, including cumene manufacture. He reports catalytic ignition temperatures for some hydrocarbons. The temperature required to provide 90 % conversion will vary depending upon the contaminant concentration and the type and amount of catalyst required for the application. The catalytic ignition temperature for 90 % conversion of benzene, toluene and xylene is about 300 °C. A typical space velocity is 75,000 m³ per



hour per m^3 of catalyst.

The catalyst is deactivated over its lifetime. The loss in activity is dependent upon the type and concentration of specific agents in the process flow in contact with the catalyst and, to a great degree, the accrual of operating time at high temperature.

Loss in activity may be due to:

- sintering
- accumulation of poisons
- accumulation of products

10.2.2 STORAGE TANKS

Petrochemical plants and refineries require large volume storage facilities for liquids and gases. In a modern plant, hydrocarbons are stored in totally enclosed storage vessels. Their type and design depend on the particular hydrocarbon to be stored and the process for which the storage facilities are provided.

Closed-storage vessels are constructed in a variety of shapes, but most common are cylinders, spheres or spheroids. Maximum capacities of pressure tanks are as much as 5,000 to 6,500 m^3 for spheres and 20,000 m^3 for spheroids. Spheres can be operated up to 1.4 MPa. Horizontal, cylindrical pressure tanks are designed with various capacities and pressures.

The most frequently used type of storage tank is a vertical, cylindrical, fixed-roof vessel with a conical or domed roof. They are usually vented to the atmosphere and therefore may represent a significant



source of hydrocarbon emissions. Up to 85 % reduction of emissions may be achieved by installation of a floating roof or internal floating cover. These modifications eliminate breathing and filling emissions by eliminating the vapor space that exists in fixed roof tanks. The application of floating roofs or internal floating covers could be applied to all storage facilities for liquids having true vapor pressures in the range of 10 to 75 kPa. A nitrogen blanket is also used for reduction of hydrocarbon losses.

Another emission control available to fixed roof tanks is a vapor recovery unit in which the vapors are liquified and returned to storage. The efficiency of such a system is dependent on the efficiency of the vapor recovery unit (28). Because of the cost of vapor recovery units, their application is limited to the more volatile materials. Yun-Chung Sun and G.R. Killat (39) described such a system as developed by Dow Chemical. It utilizes co-polymer adsorbent beads and is claimed to be suitable for control of a number of compounds: eg benzene, styrene, toluene, methylene chloride, methyl ethyl ketone, allyl chloride, pentane, hexane and gasoline. The principle of adsorption is the same as that previously described. The authors claim 100 % control efficiency for benzene at a cost lower than conventional systems (eg refrigeration or floating roof). About 3 m^3 of adsorbent can serve a 225 m^3 replacement volume per day. The superficial velocity is 1 m/min and the bed capacity is about 7 % by weight, depending on temperature. The system is adaptable to tanks using nitrogen blankets.



It is estimated that 60 to 80 % of all storage facilities in Canada utilize floating roofs or equivalents to reduce the hydrocarbon losses.

Mechanism of Storage Losses

Evaporative loss is a natural process whereby a liquid is converted to a vapor which subsequently is lost to the atmosphere. Evaporation occurs whenever a volatile hydrocarbon is in contact with a vapor space or the atmosphere. There are six basic kinds of evaporation losses from hydrocarbon storage: breathing, standing storage, filling, emptying, wetting and boiling.

Breathing losses occur when vapors are expelled from a storage tank because of temperature and/or barometric pressure changes. Standing storage losses are those resulting from leaks around latches, relief valves, and floating roof or floating cover seals. Filling losses occur when vapors are displaced to the atmosphere as a result of tank filling. Vapor expansion subsequent to product withdrawal is termed emptying loss and is due to saturation of newly inhaled air. Wetting losses are attributed to the vaporization of liquid from wetted tank walls exposed when a floating roof or floating cover is lowered by liquid withdrawal. Boiling losses occur when vapors boil off stored liquids.

The major source of hydrocarbon emissions from fixed roof tanks are breathing and filling losses, while the major source of emissions from floating roofs and internal floating covers is standing storage losses (32).



Storage emissions at petrochemical plants depend on several major factors such as liquid vapor pressure, diurnal temperature changes, schedule of tank fillings and emptyings, solar radiation absorption by the tank, and mechanical conditions of the tank (seals and fittings). The American Petroleum Institute has developed extensive formulae for calculating tank emissions (30, 31, 42). Much simplified methods are presented by other authors (32). J.W. Pervier et al (33) report losses of hydrocarbon due to storage vents in a styrene plant to be between 30 and 670 mg/kg of styrene produced. One Ontario producer (34) estimated storage and handling losses of hydrocarbons in toluene and xylene production to be around 450 mg/kg of toluene produced and 1 g/kg of xylenes respectively. R.W. Serth and T.W. Hughes (35) completed an in-depth study of air emissions from phthalic anhydride plants and estimated the storage tank emissions as follows:

Assumptions:

o-xylene temperature	23 °C
naphthalene temperature	93 °C
ambient air temperature	20 °C
breather valves set for	1 and 1.47 KPa

	Tank Capacity (m ³)	Turnovers per year	Losses kg/year
o-xylene	400	230	1,830
	4,000	23	9,280
naphthalene	4,500	1	9,300
	2,250	26	10,540
	4,500	13	14,430



10.2.3 FUGITIVE SOURCES

One of the largest, yet most difficult to control, category of hydrocarbon emissions from petrochemical processes is fugitive sources. Fugitive sources include pump seals, relief valves, pipeline valves, sampling and blind changing (32).

Pumps and compressors required to move liquids and gases can leak products at the point of contact between the moving shaft and the stationary casing. If volatile, the leaked product will evaporate to the atmosphere. The two types of seals that are commonly used in industry are packed seals and mechanical seals. The latter ones are more expensive but reduce losses significantly, usually by 90 % (32).

For safety and equipment protection, high pressure vessels are commonly equipped with relief valves to vent excessive pressure. Corrosion may cause pressure relief valves to reseal improperly, creating a potential source of hydrocarbon leaks and emissions. Surveys indicate (32) that hydrocarbon leaks from relief valves on process vessels average 1.3 kg/day-valve and from relief valves on pressure storage tanks average 0.25 kg/day-valve. Proper maintenance should greatly reduce these emissions.

Under the influence of heat, pressure, vibration, friction, and corrosion, valves and flanges generally develop leaks. The hydrocarbon emissions from these leaks depend on both the volatility of the product and the leak rate. Tests of numerous valves indicate average hydrocarbon emissions of .08 kg/day-valve (32). Again a good maintenance schedule should reduce the emissions from valves and flanges.



The operation of process units is constantly checked by routine analyses of feedstock and products. To obtain representative samples for these analyses, sampling lines must be purged, resulting in hydrocarbon vapor emissions.

There are two important factors in the control of fugitive emissions - design and maintenance. Good design, however, requires good maintenance in order to be effective. The most effective design measure to date has been the increased use of flares. The trend over the years has been to tie in all pressure-relief devices to a flare. An alternative means of controlling slowly leaking safety valves (that do not vent to a flare) is to install rupture discs ahead of the valve.

Dual sets of seals can be installed on pumps and compressors, with provision made for venting the vapors that leak past the first seal into a vapor-recovery system or a flare. Mechanical seals are gradually replacing packed seals.

Two major studies are underway to determine the fugitive hydrocarbon emissions:

- California Air Resources Board: Hydrocarbon Project (40)
- Radian Corp. for US EPA under Contract No. 68-02-2147 (41)

A study being undertaken by the Americal Petroleum Institute should also provide a method of estimating fugitive emissions with specific emphasis on storage facilities (42).

D.D. Rosebrook (37) summarizes some inexpensive and simple methods for reduction of fugitive emissions:



- replace seals, substituting mechanical seals for packed seals
- replace packing in valves, perhaps substituting packing materials or type
- replace gaskets, perhaps substituting a different material
- clean and reseal pressure-relief devices and tie them into a flare system
- cover drains
- substitute units less susceptible to fugitive emissions, such as exchanging a barometric condenser for a surface condenser
- install more modern pumps, valves, compressors, etc.



10.3 WASTE WATER EFFLUENT CONTROL

With the advent of plastic materials replacing many items in all areas of domestic, commercial and industrial applications, new problems of pollution are being developed. Various synthetic compounds are used or produced in the petrochemical industry, plastics manufacturing, solvent production, degreasing operations, textile mills, dyes and paint manufacturing, insecticides production, etc. The waste materials being generated create new challenges to technology for their disposal. One major source of pollution is the process plant itself. However, pollution could be caused by any accidental release during packaging, transport, use, and/or disposal. Many aromatic and chlorinated aromatic hydrocarbons are compounds which are very persistent in the environment.

Until recently, the approach to control of toxic pollutants in industrial waste water effluents has been governed by a set of regulations that covers the discharge of all pollutants. Even though the knowledge on toxicity of individual pollutants has improved, there is still much to learn. In many cases, data on the monitoring of discharges, analytical capabilities, toxicity of pollutants, and their persistence and degradability are incomplete or missing.

The type of compound, its physical and chemical properties, and their interrelationships will greatly affect its behaviour and fate in the environment. The most important properties from a waste water



treatability viewpoint are:

- solubility in water
- toxicity and other adverse effects on fish
- toxicity to human or animal life (See Section 13)

10.3.1 SOLUBILITY OF ORGANIC COMPOUNDS IN WATER

Table 10-1 shows the solubilities of individual compounds in water at 25 °C. For more detailed information on the physical and chemical properties of the compounds of interest here see Section 7.

Most of the chlorinated hydrocarbons, and benzene, toluene, and styrene are highly soluble in water. Naphthalene, cumene and p-dichlorobenzene are rather insoluble in water. However, all of these compounds are highly soluble in a number of solvents or oils and their solubility in waste water could be, therefore, much higher than in pure water. Solubility decreases with decreasing temperature.

10.3.2 TOXICITY TO FISH

The concentration found to be toxic to fish are listed in Table 10-2.

Naphthalene and dichlorobenzene are the most toxic compounds to fish (toxic at 5 ppm). Other compounds are generally toxic at about 20 ppm.

The compounds seem to have a narcotic effect on fish. Prior to death the fish swims wildly and erratically, but death is delayed for some time after equilibrium loss is first produced and after the fish



TABLE 10-1
SOLUBILITY OF ORGANIC COMPOUNDS IN
WATER AT 25 °C (46-49, 55)

<u>COMPOUND</u>	<u>SOLUBILITY IN WATER</u> <u>g/l</u>
Benzene	1.860
Toluene	0.500
Xylene	0.130
Naphthalene	0.040
Ethylbenzene	0.175
Styrene	0.320
Cumene	0.039
Chlorobenzene	0.448
Dichlorobenzene	
o-	0.145
m-	0.123
p-	0.079
Methyl Chloride	4.800
Methylene Chloride	20.000
Chloroform	8.220
Dichloroethane	
1,1-	5.500
1,2-	8.690
Trichloroethane	
1,1,1-	4.400
1,1,2-	4.500
Tetrachloroethane	
1,1,2,2-	2.900
Dichloroethylene	
1,1-	0.400
cis 1,2-	3.500
trans 1,2-	6.300
Trichloroethylene	1.100
Perchloroethylene	0.150
Chloroprene	N/A



TABLE 10-2

TOXICITY OF AROMATIC COMPOUNDS TO FISH

<u>COMPOUND</u>	<u>CONCENTRATION TOXIC (ppm) TO FISH</u>	<u>REFERENCE</u>
benzene	11 22 35	50 51 53
toluene	61 24 47 21	53 51 53 51
xylene	47 21	53 51
naphthalene	4-5 3	53 52
ethylbenzene	29	51
styrene	22	51
cumene	N/A	
chlorobenzene	20	51
dichlorobenzene	5	53

N/A - Not available



is immobile with only a slight twitching of the gill covers and pectorial fins.

Static bioassay tests, except those by Meyerhoff (50), and different kinds of fish were used in the tests. Since many of the compounds are highly volatile (eg benzene, toluene), the toxic concentrations could be much lower in a continuous bioassay.

"Bioaccumulation" of benzene, toluene, chlorobenzene, p-dichlorobenzene and naphthalene in different parts of the fish body has been determined by Neely (54), Chiou et al (55), Neff (56) and Lee et al (57). Bioaccumulation is defined as the ratio of the concentration of the chemical between muscle and the exposure water when measured at equilibrium. Naphthalene accumulated in fish tissue to the highest concentration. A biomagnification factor of 2.3 for naphthalene and up to 26.7 for trimethylnaphthalene has been found.

Benzene, toluene and xylene have been found in muscle and liver from fish taken close to petroleum and petrochemical waste water effluents by Ogata et al (58). The fish were offensive smelling and gas chromatographic data indicated that the offensive odor was probably due to toluene contained in petroleum industrial wastes.

10.3.3 FREE OIL REMOVAL

The choice of treatment processes for water effluents depends on the concentration of these chemicals in the water, and the nature of other contaminants which make up the total organic load in the effluent.

Large amounts of dispersed aromatic hydrocarbons and other oils



can be separated from waste water by processes generally used for removal of free oil and solids, as described by Thompson et al, 1972 (59), Gardner, 1972 (60), Quigley and Hoffman, 1967 (61), Taylor, 1973 (62), and Grutch and Mallatt, 1976 (63). By using different processes, different effluent quality could be achieved:

Effluent with >200 ppm Oil

Effluent of this quality can be expected from gravity oil-water separators. The separators may have a variety of designs and sizes according to various oil densities. Gravity oil separators will not remove emulsified oil. This separation is usually satisfactory in a system with secondary treatment.

Effluent with 50-200 ppm Oil

A well designed and carefully operated American Petroleum Institute (API) separator (Figure 10-11) can produce effluent of this quality. The addition of flocculant should be considered, particularly if a significant amount of oil is emulsified, or if an improvement in solids separation is desirable. Better quality effluent may be obtainable by using a separator larger than API design. The API separator performance varies widely and the minimum effluent oil content that can be expected is about 50 ppm.

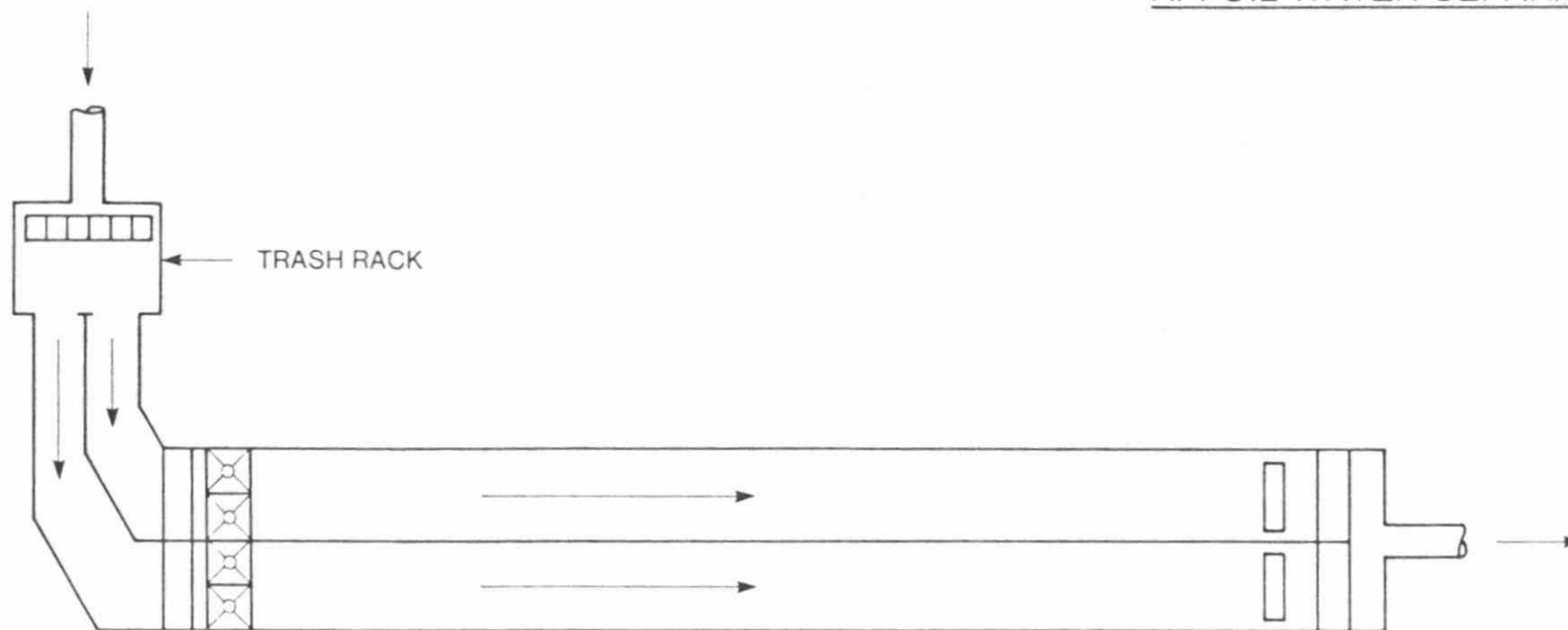
Effluent with 10-20 ppm Oil

Treatments such as induced air flotation, dissolved air flotation and filtration can produce a high quality effluent with less than 20 ppm oil.



FIGURE 10-11

API OIL WATER SEPARATOR



PLAN



ELEVATION



Induced air flotation (IAF) is a process in which air is dispersed through the waste with agitators, or venturi nozzles are provided to entrain air and disperse it into the water, to float suspended oil and solids to the surface, where the froth is removed by paddle skimmers.

In dissolved air flotation (DAF) (Figure 10-12), air is introduced into water under pressure so as to increase its solubility. When the pressure is reduced, there is an immediate release of fine bubbles of air which rise to the surface. There are many different flow arrangements and types of equipment for carrying out this operation.

Granular media filtration (Figure 10-13) is used for oil and solids suspension separation. Filter media include beds composed of sand, sand/coal, sand/coal/garnet and other minerals and synthetic materials. They can operate under gravity or pressure.

The dual media filters (DMF) (sand/coal) are the most widely used. Normal operation involves a downward flow through a bed of increasingly smaller pore size media until the pressure drop due to clogging or breakthrough of oil and solids increases to a predetermined level. The filter is then cleaned by backwashing which includes air scrubbing, reversed fluidization, and a surface wash.

The performance of all three units (IAF, DAF, DMF) is improved by using an additive. DAF and DMF usually produce an effluent of superior quality to IAF. For oil removal, DAF and DMF seems to be comparable, but suspended solids removal is much better by filtration.



FIGURE 10-12 DISSOLVED AIR FLOTATION

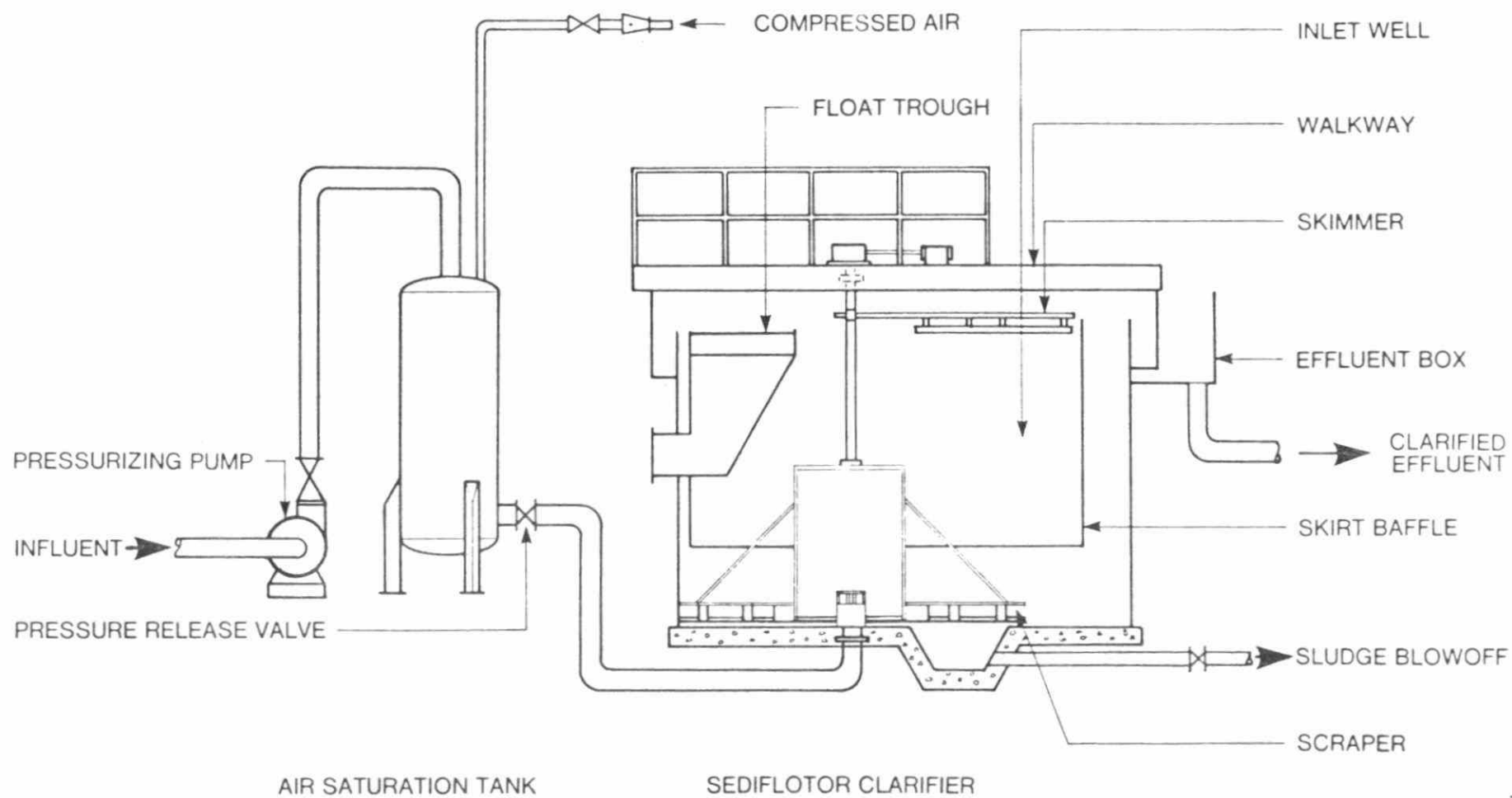
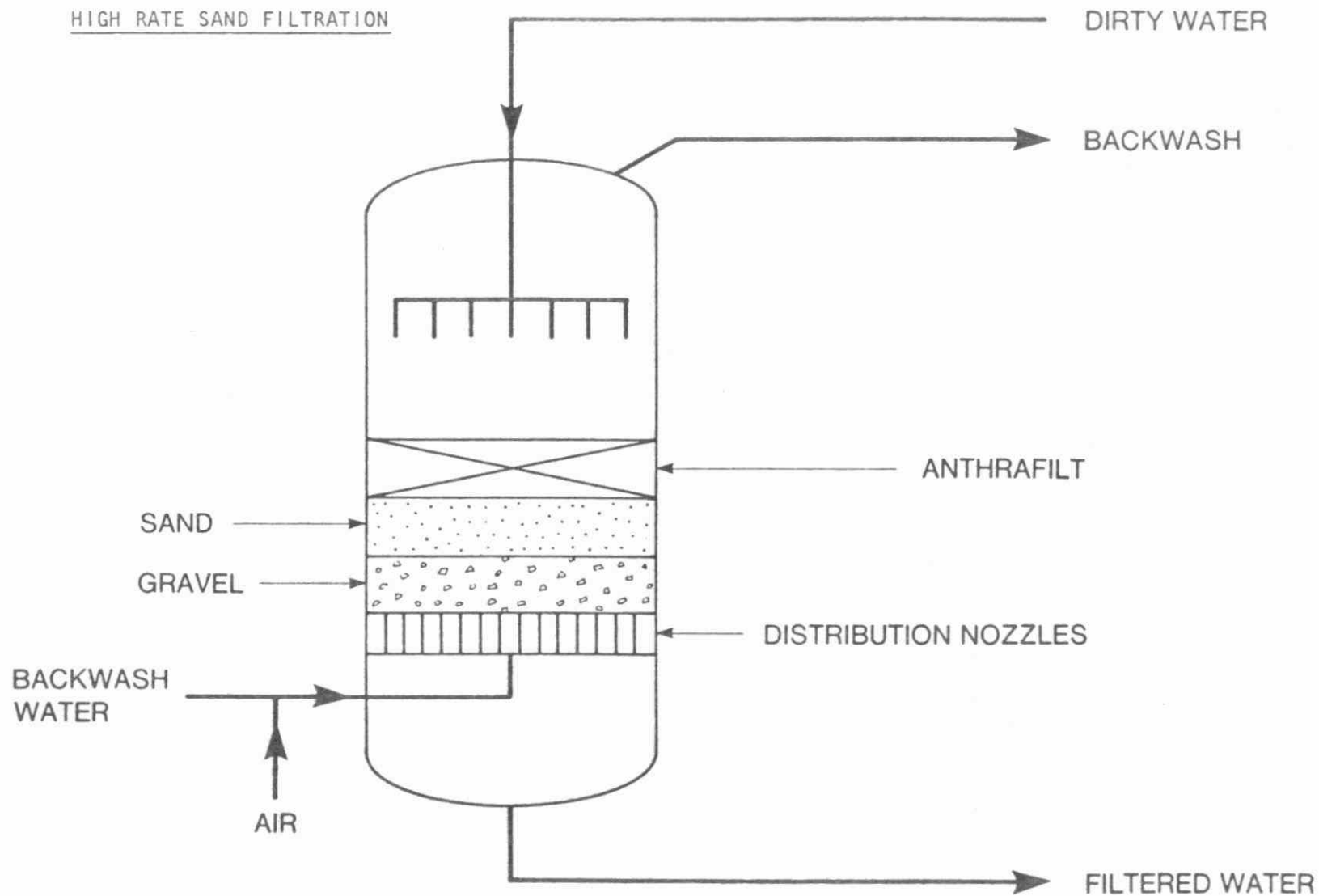




FIGURE 10-13

HIGH RATE SAND FILTRATION



Since DAF is usually cheaper than filter installation, it would normally be the process of choice for oil removal alone. However, filtration usually gives better effluent quality on waste water containing large amounts of oil. The filter backwash water requires more treatment than DAF sludge.

Effluent with <10 ppm Oil

After pretreatment to remove gross amounts of oil, effluents with less than 5 ppm of oil can be obtained from treatment such as biological oxidation or activated carbon adsorption. Studies show that these processes give excellent removal of soluble oil. When activated carbon adsorption or biological oxidation treatments are used, a major cost saving results from optimizing the pretreatment steps.

Other Treatment Methods

Concentrated solutions of toxic hydrocarbons can be disposed of by incineration (see Section 10.4) or wet-air oxidation. Many streams can be recycled to the reactors where they are converted into useful products. Another common practice is product integration. Products are recovered from the waste stream for reuse in a different plant at the same site or are shipped to another plant which has a use for them.

Wet Air Oxidation

This process is suitable for the oxidation of waste waters which have a concentration of oxidizable material of 2-20 % by weight in water. In the process, the organic matter is oxidized by air or oxygen at elevated temperature and pressure. The typical operating



conditions are 230 °C and 4.1 MPa. Good removal of dangerous toxic and obnoxious wastes and an efficient recovery of energy from relatively dilute waste streams is claimed, Ontario Research Foundation, 1977 (83).

Figure 10-14 shows the flow scheme. Waste water is pumped through the heat exchanger into a reactor. The reaction between the oxidizable material and the air proceeds autogenously. Spent air, carbon dioxide and steam are separated from the treated waste water. During the oxidation process, high molecular weight compounds are oxidized to lower molecular weight compounds which are easily biodegradable. The BOD of waste increases substantially. The degree of oxidation is a function of the reaction temperature and residence time. Operating pressure depends on the temperature and the concentration of organics.

An attractive treatment is combined wet air oxidation - biophysical treatment, Figure 10-15 (85). In this process, the organics are first partially oxidized by wet air oxidation. In the aeration basin, the waste is contacted and adsorbed on powdered activated carbon and biooxidized. Carbon and the biosludge are separated from waste water in the clarifier, returned to the aeration basin or thickened and regenerated by wet air oxidation - regeneration. Wet air oxidation is an effective and proven technology for regeneration of powdered activated carbon. Larger capacity wet air oxidation systems can be used for both oxidation treatment of waste water and regeneration of carbon. Alternatively, two separate wet air oxidation systems may be installed. An advantage of this treatment is the elimination of sludge disposal.



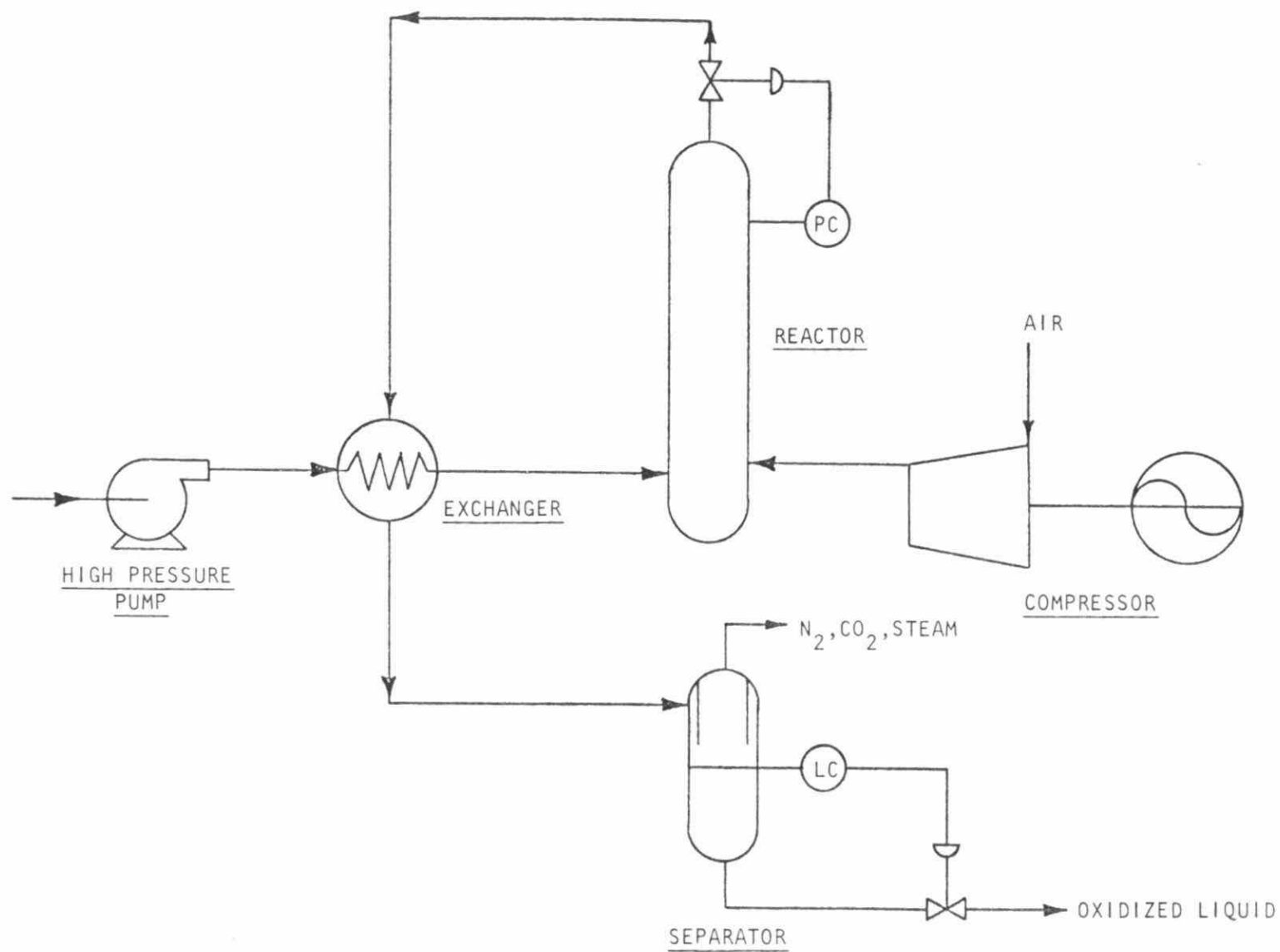


FIGURE 10-14. BASIC WET AIR OXIDATION FLOW SCHEME

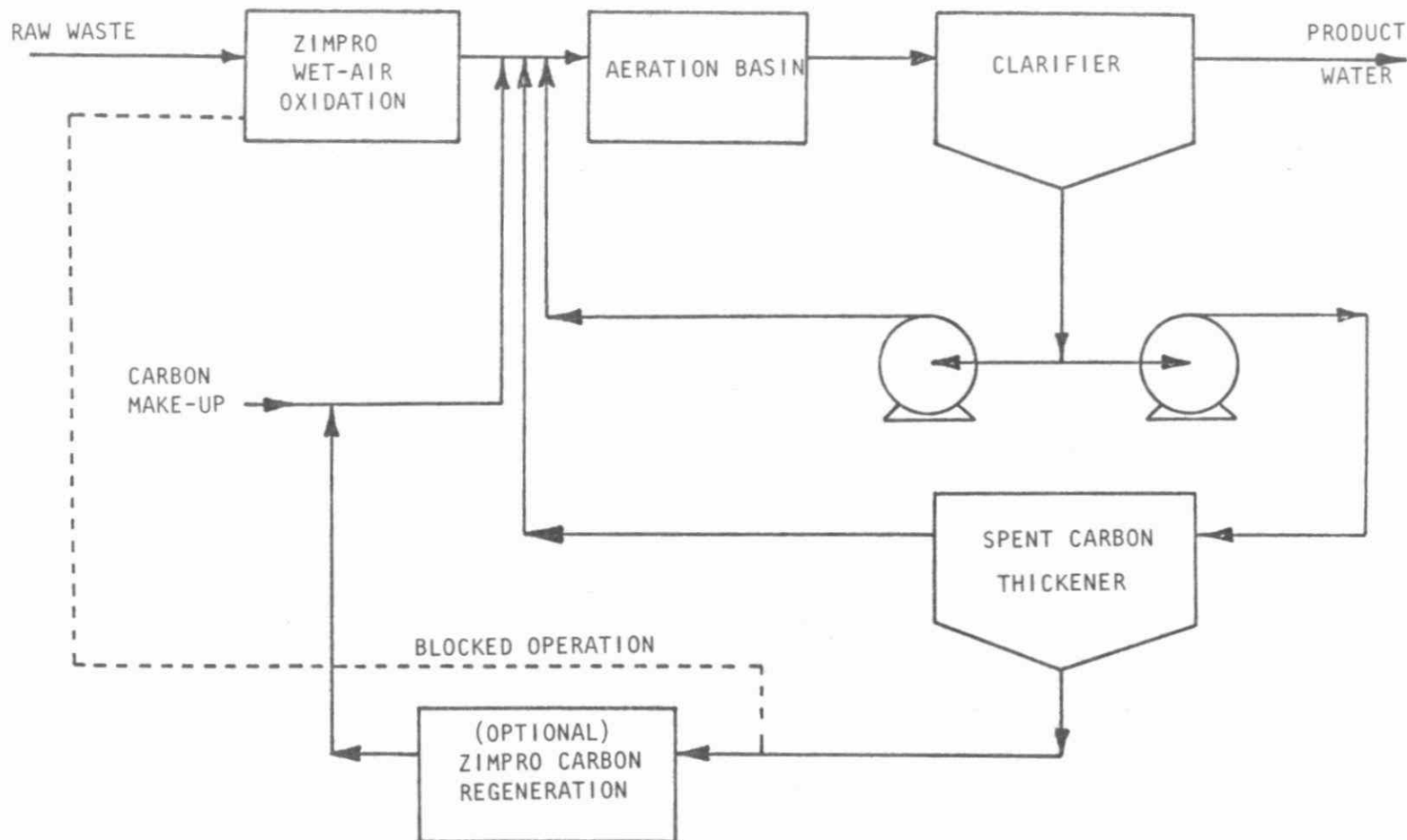


FIGURE 10-15. WET AIR OXIDATION - BIOPHYSICAL TREATMENT

Biomass associated with the carbon is destroyed during the regeneration process. The wet air oxidizes the remaining adsorbed organics and the biomass is solubilized and returned to the aeration basin in a biodegradable form.

10.3.4 SOLUBLE OIL REMOVAL

There are two possible choices for the removal of soluble aromatics from water effluents - biological oxidation or physico-chemical treatment. The type of treatment is selected according to the nature of the contaminants.

The organic load in waste water effluent has been measured by different tests. These tests are:

BOD - Biochemical Oxygen Demand is a measure of the amount of oxygen required for the complete decomposition of organic matter by microbes which grow and oxidize the organics aerobically. Historically, BOD₅ (five-day BOD) tests have been used, but also BOD₁₀, BOD₂₀ and BOD-ultimate are used with more difficult to oxidize wastes.

COD - Chemical Oxygen Demand is a measure of the oxygen equivalent of the materials present in waste water which are subject to oxidation by potassium dichromate under acid conditions. Some aromatic hydrocarbons are not oxidized in this test. Interferences result from chlorides and inorganic reducing agents.



TOC - Total Organic Carbon is the amount of carbon in the organic matter as measured by an automatic total carbon analyzer.

Biological oxidation treatment is efficient if there is a similarity between COD or TOC and BOD. Very low BOD and high TOC indicate non-biodegradable wastes or the presence of toxic pollutants. Domestic sewage has approximately $BOD_5/TOC \approx 1.85$, BOD_5 is $\sim 77\%$ of ultimate BOD and ultimate BOD is $\sim 90\%$ of the theoretical oxygen demand. Generally, the biooxidizable waste has $BOD_5/TOC = 1.35 - 2.6$. Typical petrochemical and chemical waste water effluent will consist of biodegradable and non-biodegradable organics.

The bacterial oxidation of simple aromatic and polycyclic aromatic hydrocarbons has been reported in a number of scientific publications (64-72) and a well defined pathway for bacterial degradation of the aromatic nucleus was proposed by Marr and Stone, 1961 (67) (see Figure 10-16). Oxidation of aromatic hydrocarbons appear to be more difficult and much slower than oxidation of aliphatic hydrocarbons. For example 3.5 % of benzene was found to be oxidized in 6 hours and only 13 % was oxidized in 192 hours by acclimatized activated sludge (71).

The first steps in the oxidation are apparently unique and can be carried out only by a limited number of strains of soil bacteria (*Pseudomonas*, *Achromobacter*, *Micrococcus*, *Vibrio*, *Nocardia*). Studies by Tabak, 1964 (65) show that bacteria adapted to one aromatic compound (phenol) can oxidize related compounds (benzene). In any case, the adaptation of bacteria to an aromatic compound substrate is a slow process.



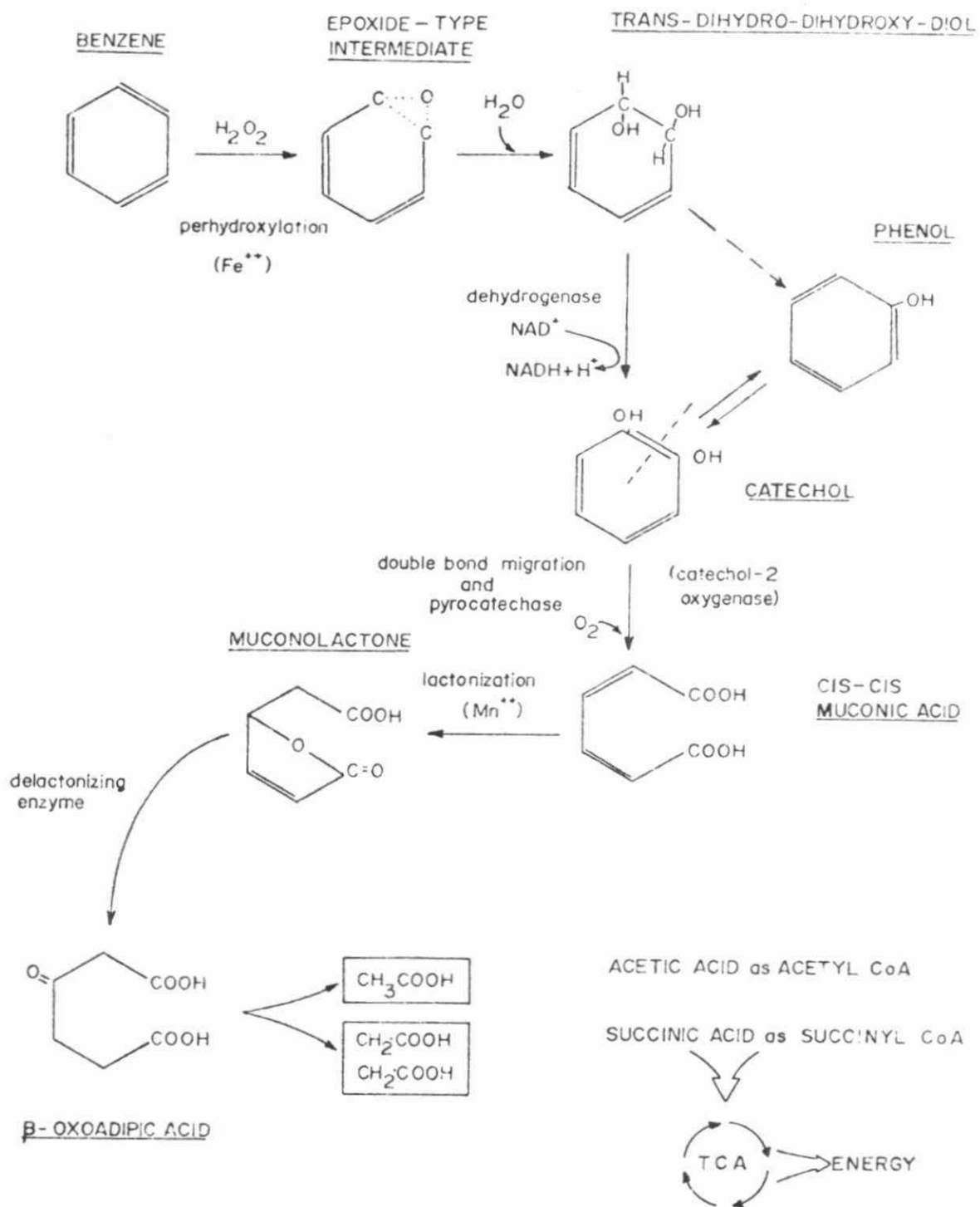


FIGURE 10-16

MICROBIAL OXIDATION OF AROMATIC COMPOUNDS



10.3.4.1 HIGH CONCENTRATION EFFLUENTS

Waste streams with a soluble organics concentration between 0.5-5 wt. % present a problem, since they are on the borderline between levels normally associated with recovery in the process plant and levels associated with waste treatment. Although conventional chemical engineering techniques such as distillation, evaporation, stripping and extraction can be used to reduce concentration of pollutants in waste water, the capital costs and energy requirement vs. desired pollution reduction rise exponentially. Membrane separation processes can theoretically produce highly concentrated streams. Perhaps development of efficient membranes will eventually allow these techniques to be used more widely. Pretreatments such as equalization, mixing, pH adjustment, flocculation/coagulation, flotation, filtration and oil separation are commonly used to prepare waste water for further treatment.

Distillation or stripping can separate compounds with appreciable vapor pressure into a more concentrated stream (81). Both processes are energy intensive. They are more expensive than evaporation.

Evaporation is a widely used technique for concentrating waste water streams containing compounds of negligible vapor pressure. The fouling tendencies of waste waters often present problems.

Extraction: Solvent extraction is an attractive and economically promising treatment for waste waters where organic load is high, recovery of organic solutes is desirable, or where the water presents special problems for biological treatment. Extraction is preferred for substances of relatively low solubility in water and sufficiently high solubility in the solvent.

Distillation or stripping are the methods used for



pollutant separation from the loaded solvent (Figure 10-17).

In the extraction process the choice of solvent is important. If the solvent does not have to be regenerated, the selection is not difficult. The most important considerations are:

- 1) Partition coefficient K_d (ppm pollutant in solvent/ppm pollutant in water). Use of the value K_d at infinite dilution for each pollutant independently is normally satisfactory.
- 2) The solvent should be highly insoluble in water.
- 3) The solvent density should be very different from that of water.
- 4) The normal boiling point of the solvent should be higher than that of the pollutant for recovery of the pollutant as a distillate. When choosing a volatile solvent, the heat economy is very important. During the distillation, all of the volatile solvent must be boiled off and then condensed.

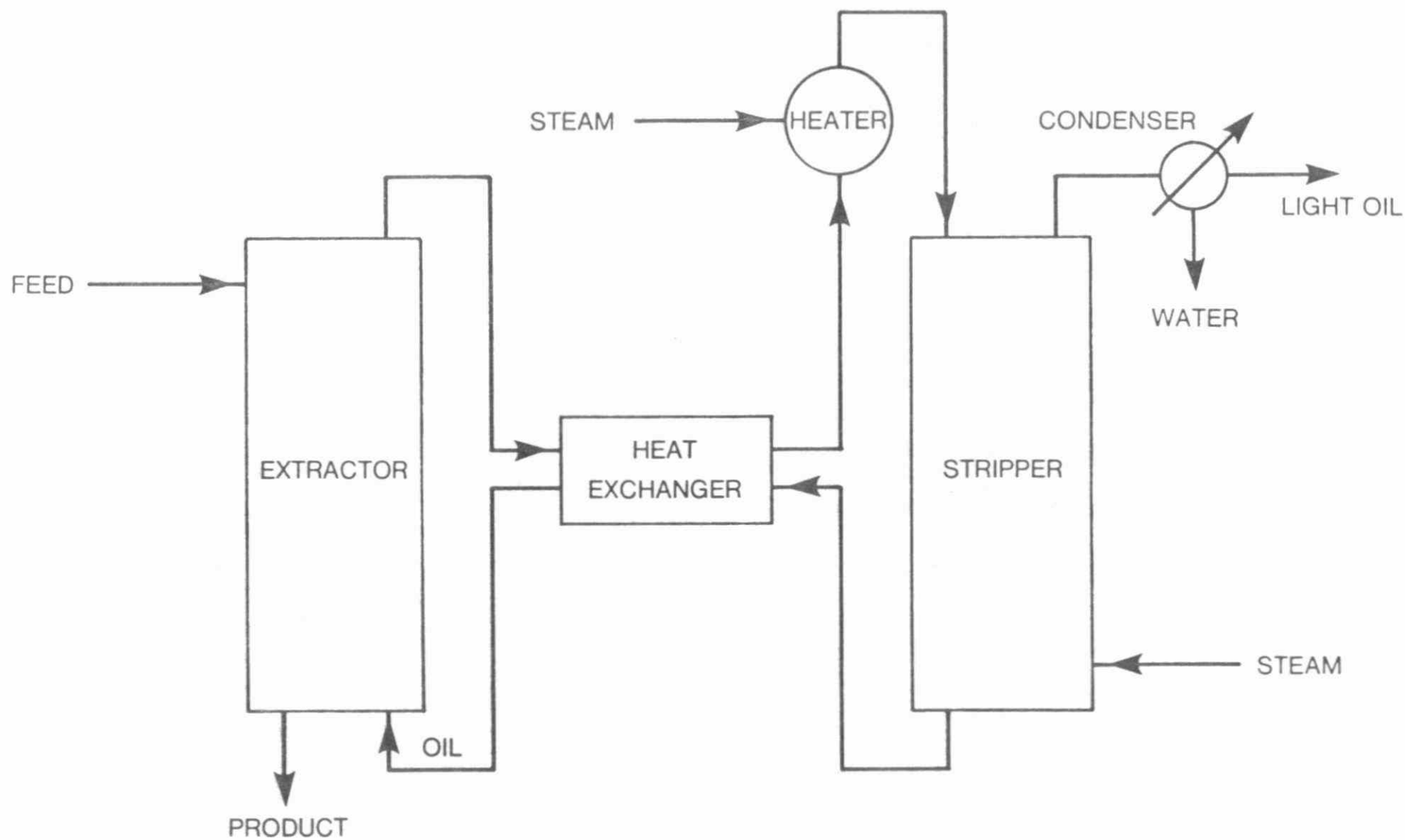
In a set of small pilot plant experiments, industrial waste water samples were tested for pollutants extraction (89):

Lube oil refining waste water containing 25-40 ppm acetone, 108-232 ppm methyl ethyl ketone (MEK), 37-107 ppm benzene, 17,000-23,200 ppm phenol and 1200-2660 ppm o-cresol was studied for extraction with the volatile solvent, isobutylene, and with the polar solvent, n-butyl acetate. The removal of





FIGURE 10-17
EXTRACTION SYSTEM



approximately 51 % acetone, 49 % MEK, 89 % phenol, 95 % o-cresol and 75 % benzene was obtained.

Ethylene quench waste water produced in a naphtha pyrolysis

olefins plant, containing 71-81 ppm benzene, 40-44 ppm toluene-, 34-40 ppm xylenes, and 67-68 ppm phenol was treated with the volatile solvents, isobutane and isobutylene. The removal of individual pollutants was 97 % for benzene, 96 % for toluene, >97 % for xylenes and 3 % for phenol.

The waste water from an oxychlorination plant which produces

ethylene dichloride contained 1.5-5.8 % HCl, 14,100-16,900 ppm chloral, 1500-3360 ppm ethyl dichloride, 290-520 ethanol, 0-100 ppm acetaldehyde and 0-300 ppm monochloro-acetaldehyde. In a dual solvent process using 2-ethyl hexanol and isobutane solvents, removal of ethylene dichloride was more than 99 %.

The waste water from a plant manufacturing styrene contained 345

ppm benzene, 170 ppm ethylbenzene and 10-20 ppm styrene. The solvent, isobutylene, removed the dissolved aromatics very effectively. The percentage removals observed were: 97 % benzene, 97 % ethylbenzene and >93 % styrene.

Membrane Processes

Membrane processes can be used for concentration and separation of toxic organics from chemical effluents. They require less energy and are compact. However, difficulties have been experienced from membrane



plugging and in maintaining membrane efficiency. More use can be expected with improvements in membranes.

Reverse Osmosis

In this process, the contaminant is physically separated from the water by circulating the solution at high pressure over the surface of a semipermeable membrane. The membrane will permit only water molecules to pass through, being impermeable to contaminant molecules. The degree of contaminant removal and the flux of purified water permeating through the membrane depends on the type of contaminant, the concentration membrane material, the temperature and the pressure head. The pressure head at equilibrium is defined as the osmotic pressure. If an external pressure is applied on the side of greater concentration, water will flow in the opposite direction; this is defined as reverse osmosis. The contaminant will concentrate in the reject stream. Extensive pretreatment of the waste water is necessary for solids and oil removal. A number of soluble organics will not only foul the membranes, but in high concentrations they will also partially dissolve it.

Thirteen pesticides, including chlorinated hydrocarbons and two metabolites of pesticides, were tested for removal by two types of the reverse osmosis membranes (eg. cellulose acetate (CA) and cross-linked polyethyleneamine NS-100) (88). With each membrane, the rejection of pesticides was better than 99 %. A considerable amount of pesticides, however, adsorbed on the membrane material. Removal of more polar pesticides was less satisfactory than removal of nonpolar pesticides



(such as chlorinated hydrocarbons).

Dialysis

This is a process which separates various compounds in solution on the basis of their molecular dimensions and the difference in chemical activity of the transferred compounds on the two sides of a membrane. The driving force is the concentration gradient, which means that with the passage of water through the membrane, the efficiency of the separation process decreases. Dialysis can be a suitable means of separation for low concentration contaminants (less than 0.1 %). Success in treating concentrated acid waste streams and good recoveries of different acids are claimed.

10.3.4.2 LOW CONCENTRATION EFFLUENTS

The treatments available for removal of toxic organics from low concentration waste water streams are: 1) biological oxidation, 2) activated carbon adsorption, 3) biophysical treatment, 4) chemical oxidation, 5) adsorption on polymeric adsorbents and 6) catalytic reduction.

10.3.4.2.1 BIOLOGICAL OXIDATION

The difficulties in oxidizing aromatics indicate that in bio-oxidation treatment a longer contact time of the substrate with microbes (sludge) is preferred and therefore, activated sludge, aerated lagoons and ponds appear to be more suitable than, for example, a trickling filter (90).

In biological treatment, organic matter is largely oxidized to carbon dioxide and water, with some being used in the synthesis of



new cells. The start-up times of biological treatment processes for systems handling organic chemical wastes are longer than for systems handling municipal wastes. Because of the extremely unfavorable reaction kinetics, staging is a common practice. For example, an aerated lagoon preceding a completely mixed activated sludge or an aerated stabilization basin preceding pure oxygen activated sludge.

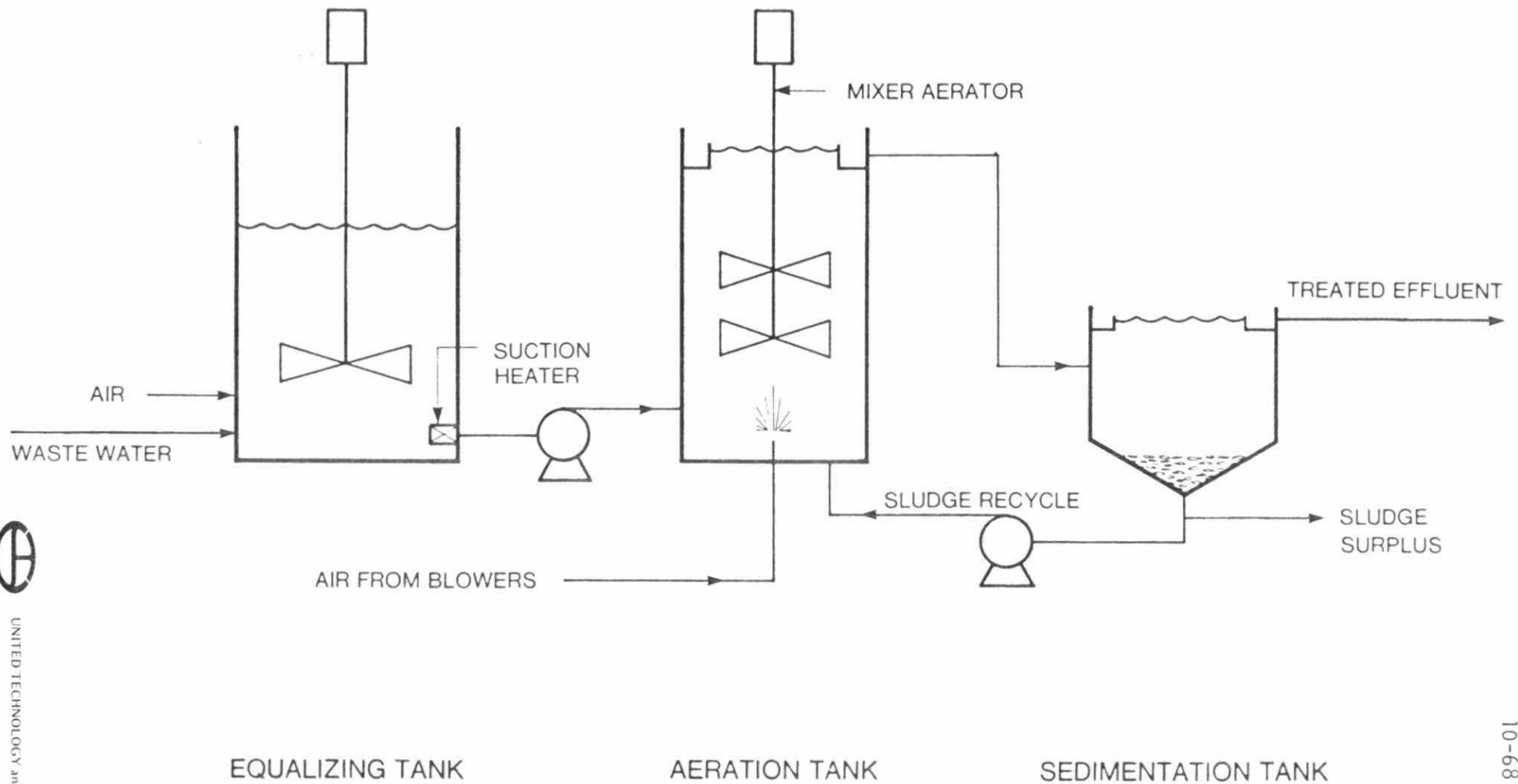
The system requires food (waste water) and oxygen (dissolved oxygen from aeration). The microorganisms feed on the organic matter in waste water, thereby reducing the strength (BOD) of the waste. The proper operation of an activated sludge plant requires that the design F/M (food to microorganisms) ratio be maintained. The F/M range for conventional activated sludge is 0.25-0.35 and, for extended aeration, 0.02-0.04. The mass of microorganisms varies from 2000-5000 mg/l of mixed liquor suspended solids (MLSS). Figure 10-18 shows the activated sludge treatment process flowchart. After equalizing in the equalizing tank, the waste water is contacted with sludge in the aeration tank. In the sedimentation tank, the sludge is separated from the waste water, part of the sludge being returned to the aeration tank. Surplus sludge is wasted.

Where a high rate of organics removal is required, some type of activated sludge unit is the most practical solution. All types of high rate activated sludge units are sensitive to shock loads and therefore must be protected. The usual method is to use equalizing tanks for the feed.



FIGURE 10-18

ACTIVATED SLUDGE TREATMENT



Activated sludge treatment is not recommended for wastes containing a large concentration of highly volatile aromatics (benzene, toluene), due to the danger of creating an odor problem. Also, if the sludge is not enriched with the aromatic hydrocarbon oxidizing microbe, the compound could go through the treatment unchanged and then need to be removed in a polishing treatment step.

Activated Sludge Process

The activated sludge process may be briefly described as a system in which a large number of biological organisms are maintained and continuously circulated so as to be in constant contact with the organic waste water in the presence of oxygen.

Trickling Filter

This is a bed filled with rocks or synthetic media, 1-5 m deep. The media provide surfaces for biological sludge growth. The organic material is oxidized as the water flows through. The organic load ranges from 2.3-11.4 kg for high rate filters.

The advantage of this process is the ability to cope with shock loading. In general, materials toxic to bacteria in the activated sludge will be toxic to a trickling filter. It is not recommended that a trickling filter be used as a single stage treatment but that it be installed as a roughing device or first stage biological treatment.

Aerated Lagoon

This is a basin 2-6 m deep in which the incoming waste water is contacted for long periods of time with a dispersed biological growth. Aeration is provided by mechanical or diffused aeration equipment. In



the aerated lagoon for treating synthetic organics at a Union Carbide Plant, the reduction of naphthalene, styrene and toluene was 70-90 % and benzene 9-100 %. The plant operates with 74-90 kg/day/1000 m³ BOD load and 155-181 kg/day/1000 m³ COD load and 66 hours retention time. The overall removal of BOD was ~50 % and of COD ~40 %. It is recommended that an aerated lagoon be used as an equalization tank or a polishing pond.

Oxidation Ponds

These are large shallow (~1.2 m) basins. Aeration is accomplished by natural surface reaeration and algal photosynthesis. Retention times in the ponds range from a few days to 3 months. Ponds are used for polishing the effluent from biological waste treatment processes. It is recommended that typical BOD loadings ranging from 9-45 kg BOD₅/acre/day for raw waste and 4.5 kg BOD₅/acre/day for polishing waste effluents be used. Reported BOD removal efficiencies are 60-90 %.

10.3.4.2.2 ACTIVATED CARBON ADSORPTION

Activated carbon adsorption is the most up-to-date method and is receiving more and more attention from municipalities and industries for use in the removal of organic compounds that are not readily biodegradable, are toxic to fish, or produce taste, color or odor in waste waters.

Activated carbon has a highly porous structure of very large surface area, 500 to 1200 m²/g, which provides many sites upon which adsorption of molecules can take place. The average pore size is small, around 3 μm, and the distribution of pore sizes is quite wide. The adsorption of organics is a results of physical and chemical forces. Physical adsorption



results from molecular condensation in the capillaries of the carbon particle, and chemical adsorption results from a chemical bond between the carbon surface and organic molecule. The rate of adsorption is controlled by the rate of diffusion of the soluble molecules into the capillary pores of the carbon particles. An adsorption equilibrium is established when the concentration of contaminant remaining in solution is in a dynamic balance with that at the surface. Adsorption capacity will increase with increasing concentration of contaminant in solution and with its decreasing solubility in solution. The adsorption phenomena is usually expressed by the Freundlich isotherm:

$$X/M = kC^{1/n}$$

X - weight of contaminant adsorbed

M - weight of adsorbent (carbon)

C - concentration of contaminant remaining in solution

k, n - constants depending on temperature, adsorbent and the substance to be adsorbed.

Both organic and inorganic compounds can be adsorbed. Adsorbability of different organic components varies widely with molecular size, structure, branching, solubility, polarity, pH and other factors. Table 10-3 shows the influence of molecular structure and other factors on adsorbability, as presented by Ford, 1972 (76). Generally, nonpolar aromatic hydrocarbons of low molecular weight, such as benzene, are highly adsorbable on carbon. The aromatics are capable of π -bonding



TABLE 10-3
INFLUENCE OF MOLECULAR STRUCTURE AND
OTHER FACTORS ON ADSORBABILITY

1. Aromatic compounds are generally more adsorbable than aliphatic compounds of similar molecular size.
2. Branched chains are usually more adsorbable than straight chains.
3. Substituent groups affect adsorbability:

<u>Substituent Group</u>	<u>Nature of Influence</u>
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic are more adsorbable than acetic but similar increases do not occur when introduced into higher fatty acids.
Double bonds	Variable effect.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.
4. An increasing solubility of the solute in the liquid carrier decreases its adsorbability.
5. Generally, strongly ionized solutions are not as adsorbable as weakly ionized ones; ie, undissociated molecules are in general preferentially adsorbed.
6. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.
7. Unless the screening action of the carbon pores intervene, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute-carbon chemical bonds being formed, making desorption more difficult.



with the surface of the activated carbon, which has been found to be aromatic in nature.

There is very little information in the literature on the adsorbability of specific compounds. The most comprehensive study on adsorbability of pure compounds from ten functional groups commonly found in petrochemical effluents was given by Giusti et al, 1974 (74). In this study, the removal of benzene was 95 %, toluene 79.2 %, ethylbenzene 84.3 % and styrene 88.8 %. Ninety-five percent removal of benzene was also found by Scherm and Lawson, 1976 (73). High adsorbability was predicted for toluene and chlorobenzene by Rizzo and Shepherd, 1977 (75).

The effectiveness of activated carbon adsorption treatment for industrial waste waters is usually measured by removal of organics (TOC), COD, color or toxicity. Waste water effluents often contain a number of contaminants and are too complex to characterise. Hagar, 1973 (77) surveyed 222 adsorption isotherms of waste water from 68 industries. The results of this survey show that activated carbon adsorption reduced TOC by more than 90 % in 10 samples, 85-90 % in 29 samples and less than 85 % in 53 samples. The TOC was used in these studies because it is a better measure of adsorption performance than COD or BOD. Chemical clarification, oil flotation and filtration were common pretreatment processes.

Experience shows that not all organics adsorb completely in a multicomponent system such as petrochemical effluent. While aromatics are reported to be relatively efficiently adsorbed, Scherm and Lawson, 1976 (73), some low molecular weight oxygenated organics have only



limited adsorbability. Competition for adsorption sites and mutual solubility may result in the leakage of some aromatics in the effluent. Also, since adsorption on carbon is dependent on the dynamic concentration equilibrium, unloading and leakage are likely to occur in the periods following extremely high concentrations of organics in the feed to the carbon bed (eg spills).

Fixed-bed and expanded-bed carbon adsorbers are commonly used for continuous treatment. Waste water is applied to the beds at rates generally ranging from 2 gpm/ft² and 8 gpm/ft² (81-326 l/min/m²). Lower flow rates are used in downflow gravity packed beds. Higher flows are used in expanded-bed upflow adsorbers. An essentially equivalent adsorption efficiency is obtained from equivalent contact time. Contact times employed are in the range of 30 to 60 minutes on an empty bed basis.

By passing waste water upward through the bed of carbon at velocities sufficient to expand the bed, problems of fouling, plugging and increasing pressure drop are minimized.

Biological growth on the surfaces of the carbon can present some problems in packed bed adsorbers. Effective control of biological growth can be accomplished by regular chlorination of the feed to the adsorbers or by chlorination during backwashing. Anaerobic conditions and H₂S production are controlled by aeration of the feed. Regular backwashing and air scouring should be provided to remove solids and biological growth. Granular carbon has been used in most systems because of the relative ease of handling and regenerating.



Due to the complexity of industrial effluents and the high cost of activated carbon adsorption treatment, the feasibility of its use should be determined by both carbon adsorption isotherm and continuous flow pilot plant simulation tests.

Carbon Adsorption Isotherm

To determine the isotherm, contaminated water is contacted with a series of known weights of pulverized carbon and agitated at a constant temperature. After the adsorption equilibrium is reached, the carbon is removed and the residual concentration of contaminants measured. The test data are plotted on a log-log scale representing the isothermal relationship between contaminant concentration and carbon equilibrium capacity. Figure 10-19 shows different types of Freundlich isotherms, Ford, 1972 (76). The isotherm is used to estimate carbon capacity. However, the data should not be used for design purposes since the isotherm represents only an ideal system.

Pilot Plant Tests

Continuous pilot plant tests, preferably on site, are necessary to investigate the effect of the variability of plant conditions, spills and possible leakage of contaminants from carbon columns. Columns 2-8 inches (5-20 cm) in diameter and 5-8 feet (1.5-2.4 m) in height, usually connected in series (upflow or downflow) are used in the tests (Figure 10-20). Facilities for backwashing should also be provided.

Pilot plant tests determine the contact times necessary for contaminant removal, the amount of carbon consumed per unit volume of liquid treated (service time of the bed), and the required regeneration frequency



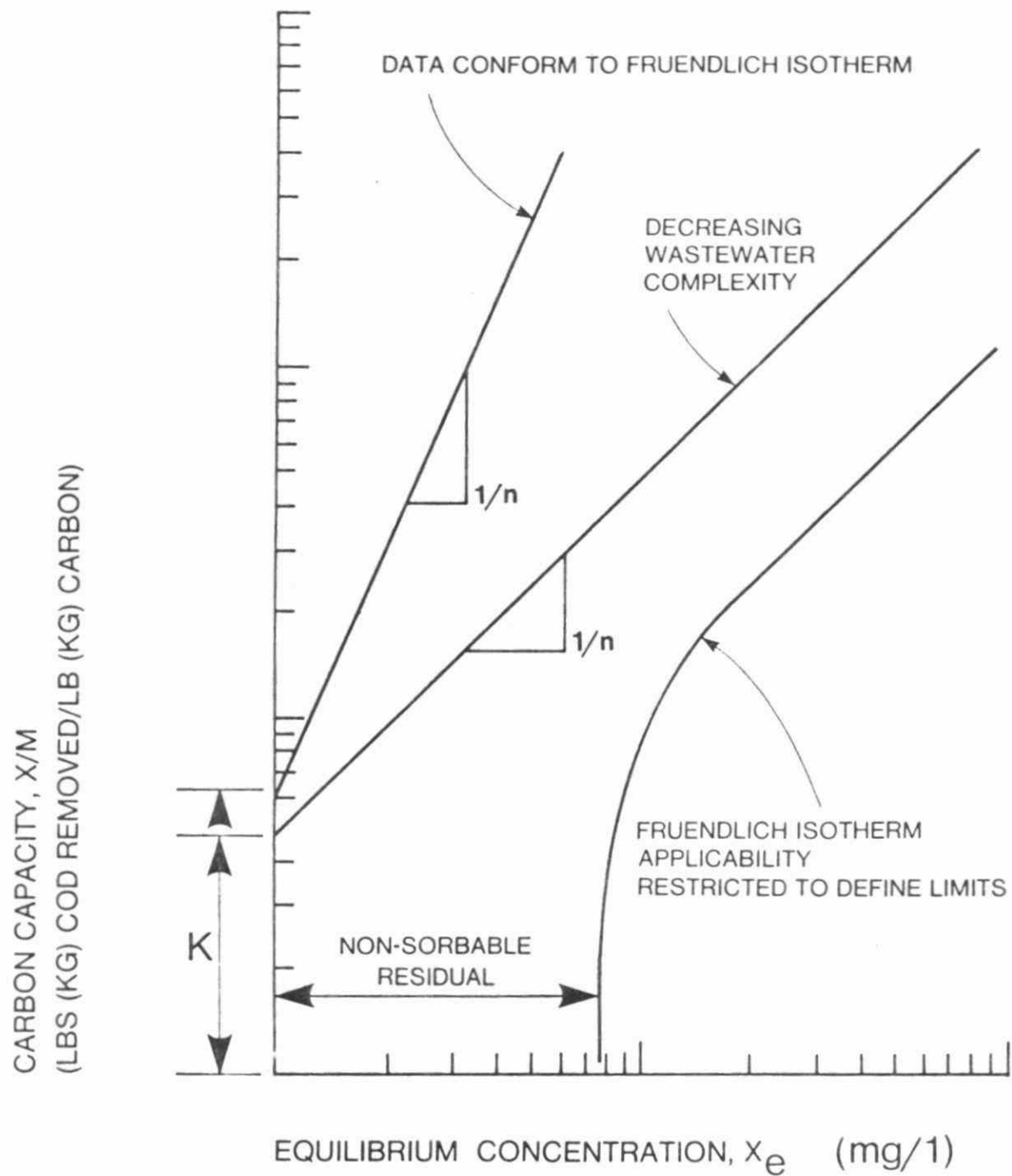


FIGURE 10-19

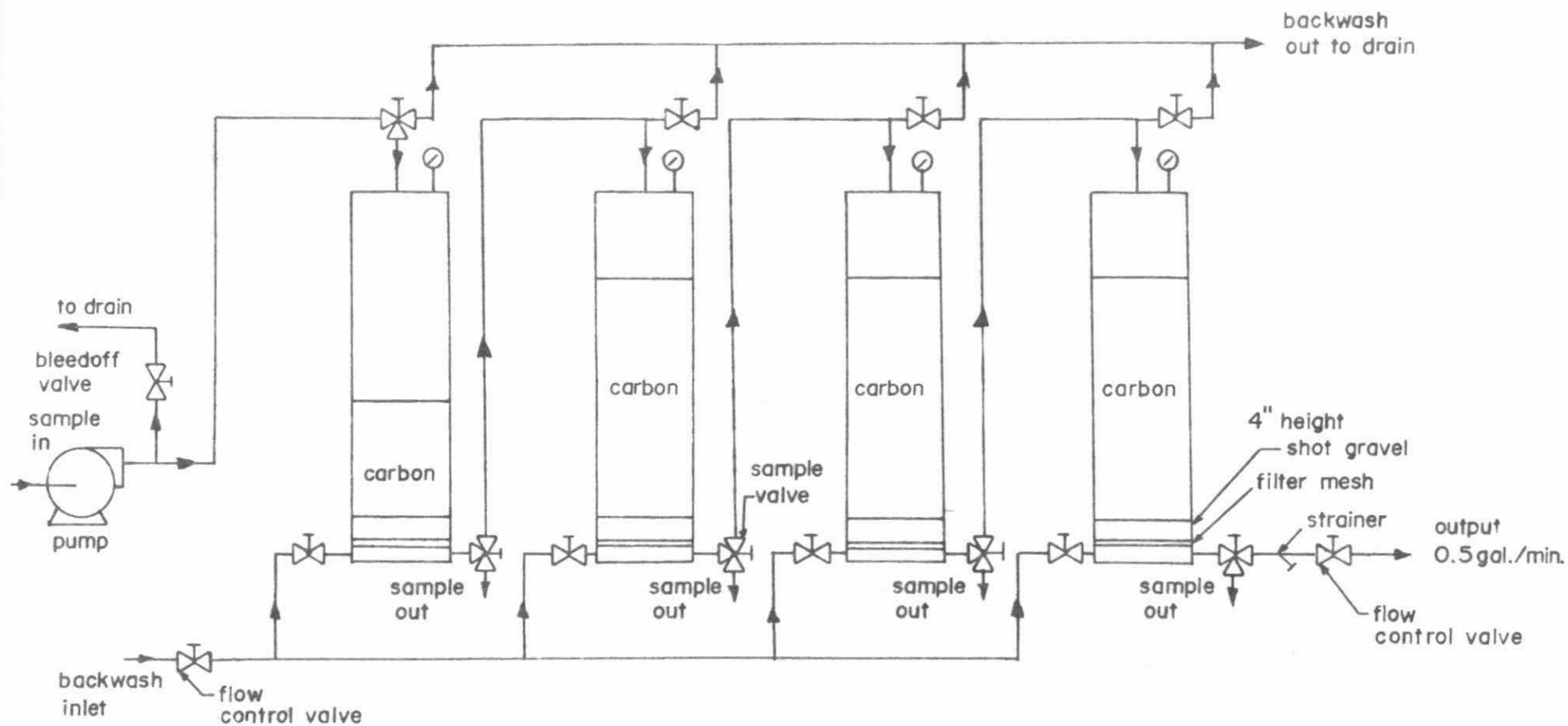


FIGURE 10-20

SCHEMATIC OF PILOT PLANT FOR CARBON ADSORPTION TESTING

for carbon. Long carbon contact time and low surface velocity increase the effluent quality and carbon bed service life.

From the columnar study a breakthrough curve is constructed and all necessary data calculated. Figure 10-21 shows an ideal breakthrough curve (water of a constant composition) and Figure 10-22 shows experimental breakthrough curves for a system with two beds in series, Scherm and Lawson, 1976 (73).

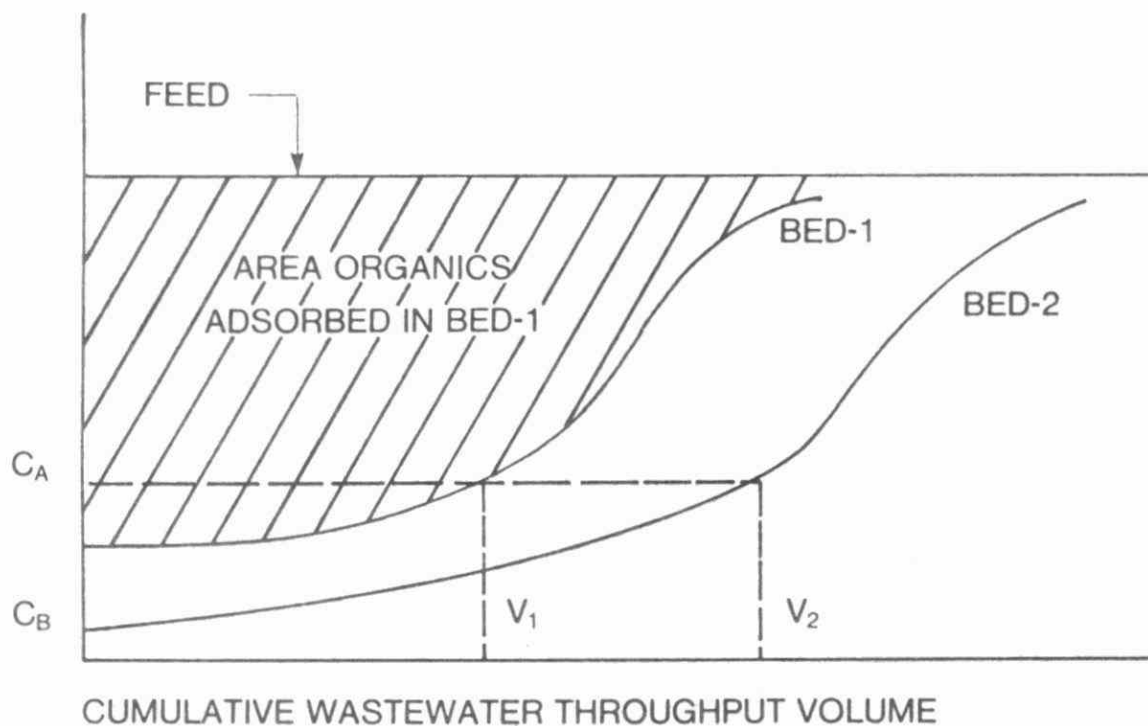
There are four options regarding the handling of carbon after it has been exhausted:

- a) Throwaway Carbon: Virgin carbon is charged into the adsorbers. When it becomes exhausted it is removed and disposed of by landfilling.
- b) Offsite Reactivation: Carbon is shipped to an offsite reactivation facility for thermal reactivation.
- c) Onsite Reactivation: A multi-hearth furnace or rotary kiln is used to thermally reactivate spent carbon (Figure 10-23).
- d) Adsorption Service: Service by carbon producing company for adsorption equipment and carbon handling.

Addition of powdered activated carbon improves activated sludge treatment because of the carbon adsorptive and physical properties, Perrotti and Rodman, 1973 (78), Davis, 1977 (79), DeJohn and Adams, 1975 (80). Organics and oxygen are adsorbed, which results in their increased concentration on the carbon surface. This enhances biological



ORGANIC CONCENTRATION (COD)



C_A = TARGET EFFLUENT ORGANIC CONCENTRATION

C_B = MINIMUM ACHIEVABLE EFFLUENT CONCENTRATION
(INDICATES "LEAKAGE" OF ORGANIC COMPOUNDS
WHICH ARE ESSENTIALLY NON-ADSORBABLE,
OR WEAKLY ADSORBED)

V_1 = CUMULATIVE WASTEWATER THROUGHPUT AT
BREAKTHROUGH OF COLUMN 1

V_2 = CUMULATIVE WASTEWATER THROUGHPUT AT
BREAKTHROUGH OF COLUMN 2

FIGURE 10-21

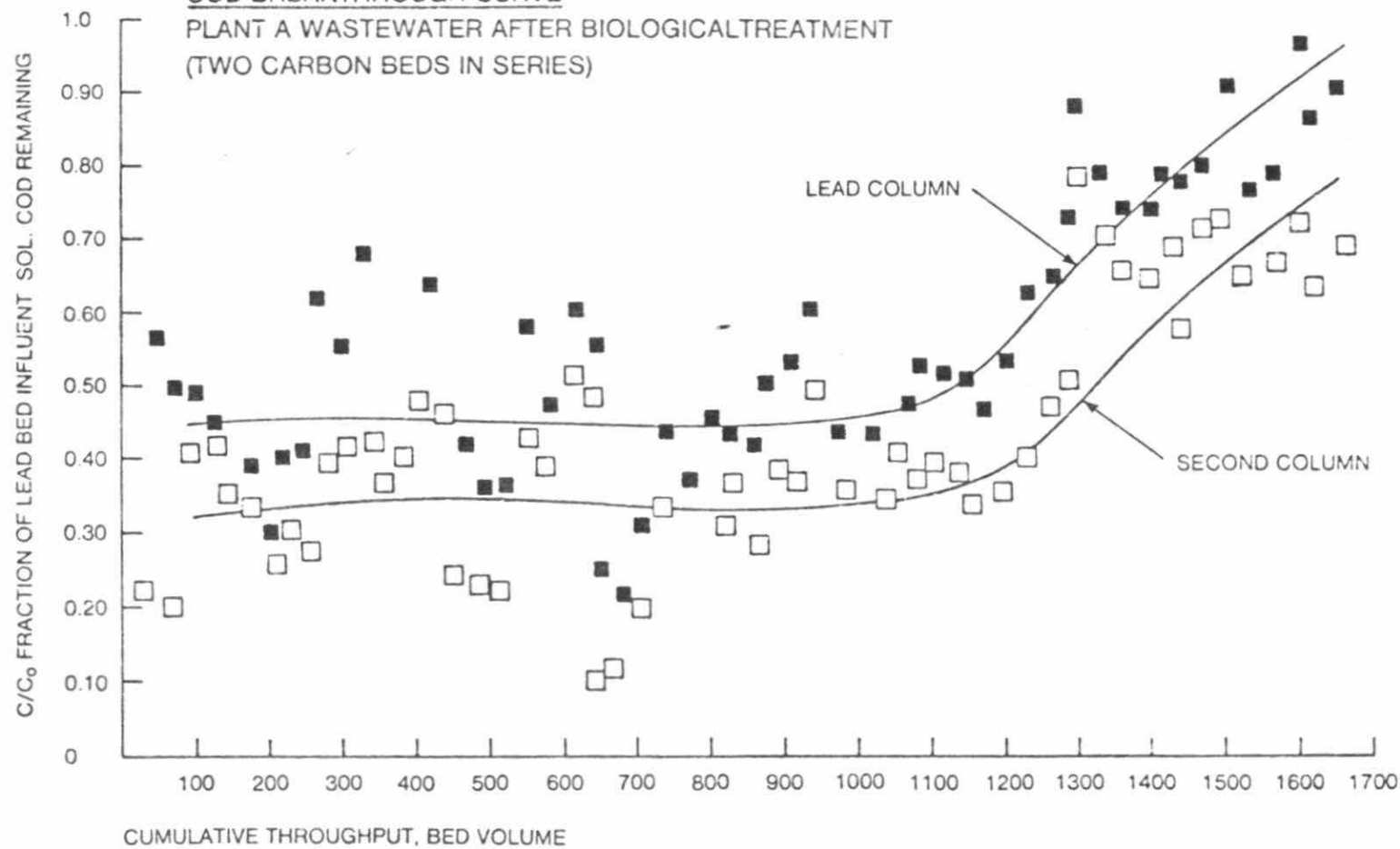
IDEAL BREAKTHROUGH CURVE FOR ACTIVATED CARBON



FIGURE 10-22

COD BREAKTHROUGH CURVE

PLANT A WASTEWATER AFTER BIOLOGICAL TREATMENT
(TWO CARBON BEDS IN SERIES)



BASED ON VOLUME OF ONE BED = 5.7 LITERS/BV



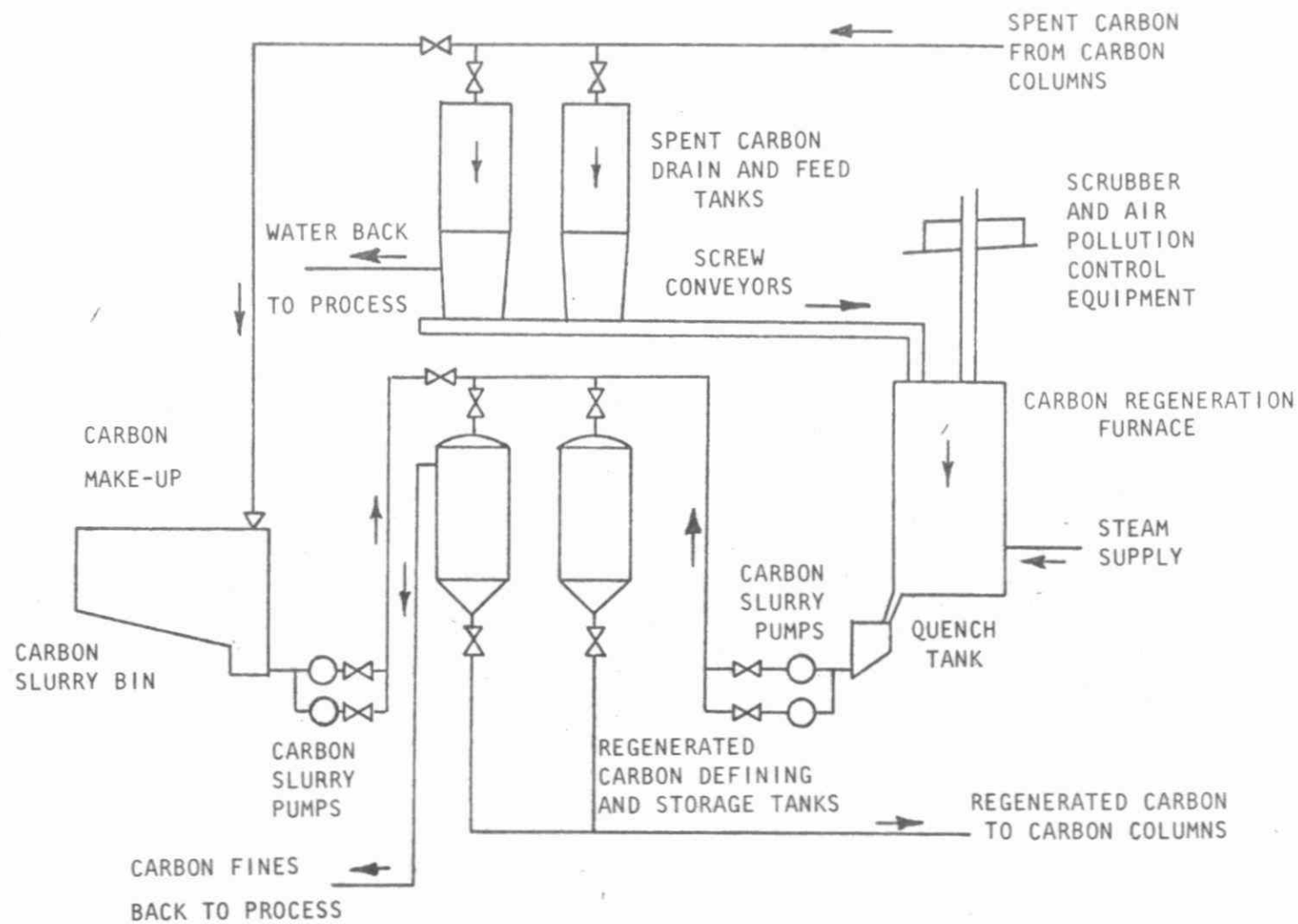


FIGURE 10-23. SCHEMATIC OF CARBON REGENERATION SYSTEM

oxidation and degradation of organics which may require a longer contact time with the biomass. Effluent COD, BOD and TOC are usually lower than without carbon addition. High density powdered carbon improves solids settling and prevents foaming. The sludge is thicker and more easily dried.

In an activated sludge containing 1000-2000 mg/l of biological solids, carbon is added to the effluent at a concentration of less than 100 g/l. The carbon is then recirculated and purged along with the sludge. The Zimpro Co. Inc. feels that the "biophysical" treatment of the effluent from a wet air oxidation process has great applicability to the treatment of toxic industrial wastes where the toxic refractory substances have survived wet air oxidation treatment and might be either toxic to the conventional activated sludge or are very slowly biodegradable (85). This process differs little from a conventional activated sludge process, except that the powdered activated carbon concentration in the aeration basin is in excess of 10,000-20,000 mg/l at the same time as the active biomass concentration is 10,000-15,000 mg/l of suspended solids. These high concentrations allow smaller aeration basins, longer sludge life, lower sludge production and rapid settling. Carbon also greatly reduces odor from the aeration basin when treating waste with volatile odorous organics. Figure 10-24 shows the flow diagram of a biophysical treatment process.

Placement of Carbon Adsorption within Water Treatment

The efficiency of activated carbon (AC) adsorption and its placement



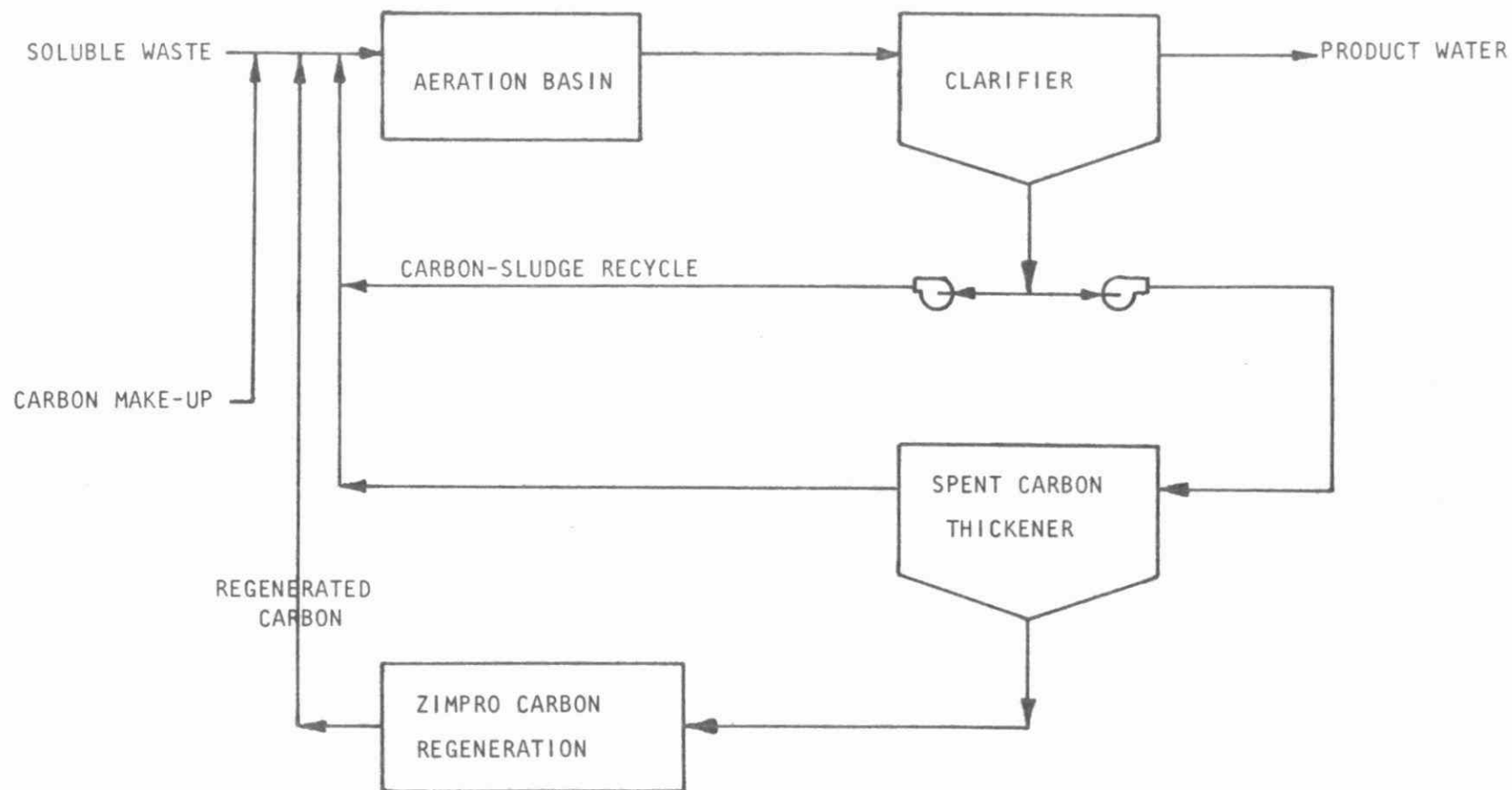


FIGURE 10-24. FLOW DIAGRAM OF BIOPHYSICAL TREATMENT

at any point in a treatment process can be determined only after a thorough investigation. Granular activated carbon adsorption - filtration can be placed prior to, or after, biological treatment, or as a total treatment process (Figure 10-25, Ford, 1972 (76)).

Biological oxidation treatment followed by AC adsorption seems to be the most attractive control process for the near future. AC adsorption works as a polishing tertiary treatment where the effluent from secondary bio-oxidation treatment does not meet the effluent quality criteria or for where refractory, hazardous and toxic organics are not removed by the secondary treatment stage.

Activated carbon adsorption could be placed prior to bio-oxidation treatment to remove biotoxic organics or for removal of occasionally high concentrations of organics which could upset the bio-oxidation treatment. Although this system has the apparent advantage of a more effective use of carbon adsorption, the final effluent has all the disadvantages of secondary biological treatment: high solids, color, less effective bio-oxidation.

Application of activated carbon adsorption as a secondary treatment is possible only in special cases. It can be used for the removal of non-bio-oxidizable or very slowly oxidizable organics, but not for TOC removal. However, the criterion is that these organics be highly adsorbable on carbon. "Leakage" of low concentration of other organics can be expected.

An economical use of AC adsorption can also be in the upstream removal of a high concentration of a single contaminant. This can be particularly useful in the case of relatively highly soluble, but still



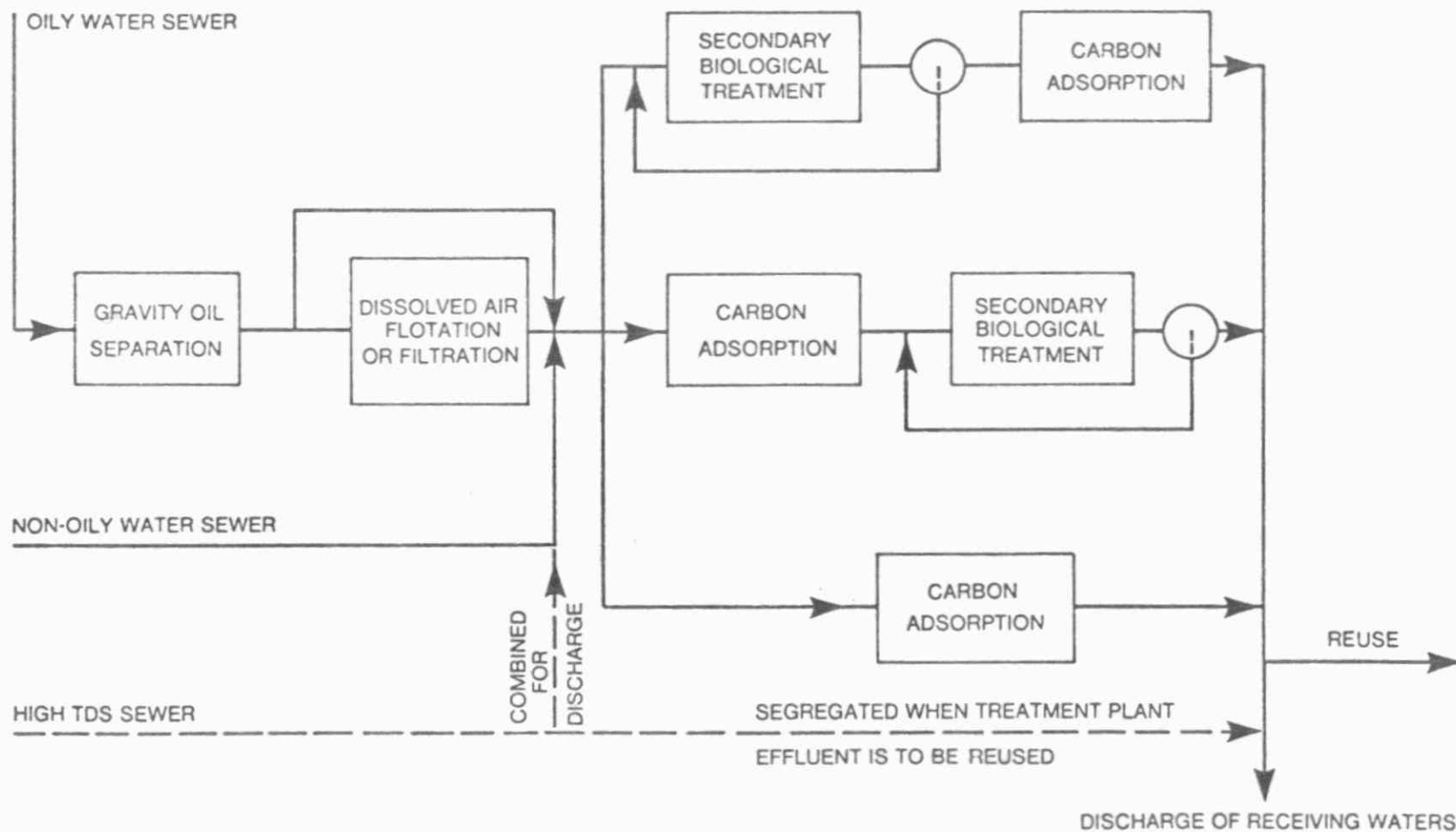


FIGURE 10-25

CANDIDATE SYSTEM APPLICATION FOR CARBON COLUMNS WITHIN A REFINERY TREATMENT COMPLEX

highly adsorbable compounds, such as benzene.

The use of powdered AC is limited today to its addition into activated sludge treatment. Though it does not produce as good an effluent quality as from biological treatment followed by AC adsorption, it may improve removal of organics, reduce solids in the effluent, improve sludge settling, and remove some refractory organics such as detergents, dyes, etc.

10.3.4.2.3 OTHER TREATMENT METHODS

Chemical Oxidation

Various oxidants have been used for the oxidation of nonbiodegradable organics. Disinfection with chlorine is the approved practise for treating municipal drinking water supplies. However, recently, chlorinated organics have been detected in drinking water from such treatment plants and has lead to the search for a suitable alternative to chlorination.

Ozone is a stronger oxidant than chlorine. It seems to be quite effective in oxidizing high-molecular weight organics that are otherwise difficult to treat. Typical O_3 reaction products are carbonyls, glycols, and acids, along with products of aromatic benzene ring cleavage. The organic oxidation products are largely biodegradable. Ozone with UV treatment reduces the concentration of various pesticides to near zero (86) and works effectively on chlorinated hydrocarbons such as pentachlorophenol, dichlorobutane, dichlorobenzene and chloroform.

Calcium Hypochlorite may be more suitable as a water disinfectant than chlorine. There is an indication that hypochlorite does not produce



haloforms such as chloroform in treated waters. Also, this chemical functions as an algicide in cooling water systems.

Polymeric Adsorbents

A new separation technique has been developed by the Rohm and Haas Company using new macroreticular polymeric adsorbents that are used specifically for adsorbing aromatic and aliphatic compounds from water. Nonionic compounds such as benzene or naphthalene are reported to be removed with 100 % efficiency, Simpons, 1972 (82).

Another polymeric adsorbent was discovered by Union Carbide researchers. The adsorbent is a highly stable molecular sieve material, a polymorph of silica (SiO_2) called silicalite (91). Besides its adsorbent ability, the surface of this material preferentially adsorbs nonpolar organic molecules and repels water molecules. It can adsorb any molecule the size of benzene and smaller. The material seems to be remarkably stable to very high temperatures (up to 1100 °C), which would be very useful for regeneration.

Catalytic Reduction

A catalyzed-iron reducing agent has been reported to successfully reduce small amounts of chlorinated hydrocarbons (87). The reduction column contains catalyzed iron powder reductant (100-200 mesh) in a sand-bed matrix. Figure 10-26 shows the flow chart of the treatment. Pretreatments such as filtration for oil and solids removal, pH adjustment, etc. should be used. Reduction of chlorinated pesticides from 100 ppb-1 ppm to 1-10 ppb, and of polychlorinated biphenyl (PCB) from 200 ppb to less than 1 ppb was obtained in a field test. The



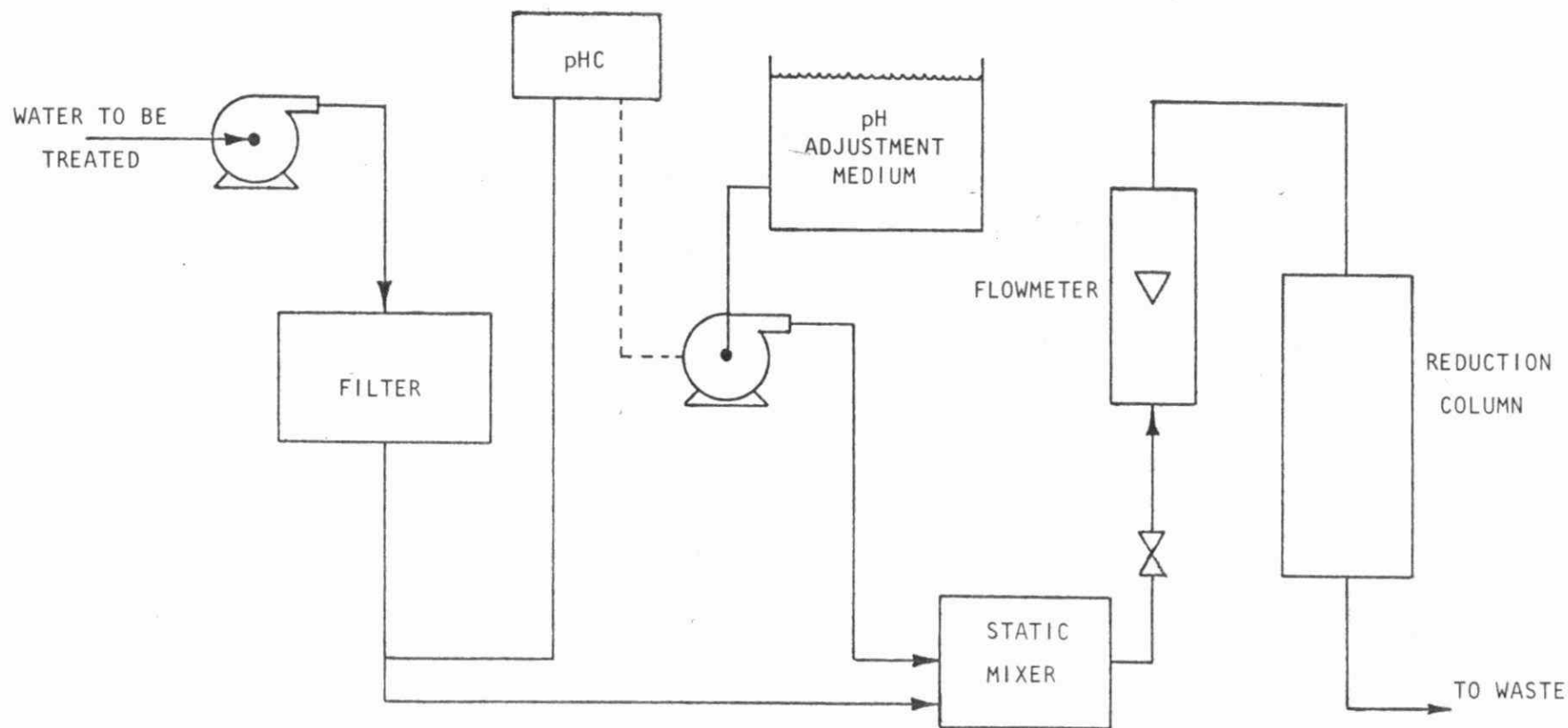


FIGURE 10-26. REMOVAL OF CHLORINATED HYDROCARBONS BY CATALYZED-IRON REDUCING AGENT



indications are that the system can also remove "light ends" such as chloroform, carbon tetrachloride and ethylene dichloride.



10.4 WASTE DISPOSAL METHODS

For the purpose of this report "waste" is defined as a solid or concentrated liquid material which cannot be further processed for recovery of valuable components and has to be disposed of by means of destruction to harmless compounds or stored in such a way that it is prevented from entering the environment.

Deep wells and land fills have often been used in the past to dispose of chemical wastes. However, it has become more and more difficult to find sites for disposal where there is no risk of ground water contamination. In some countries, burial of oily wastes has already been banned and it is virtually certain that such disposal will be severely restricted in most countries in the future (92).

With the latest processing technology, the production of waste in petrochemical plants is minimized. However, for this very reason, information on quantities of wastes produced and operationing parameters is not available. Incineration is considered an ultimate disposal method for refinery and petrochemical wastes.

10.4.1 INCINERATION

Incineration is one method used for the destruction of wastes containing liquid and solid organic compounds. The principal products of combustion of organic materials are carbon dioxide, water and ash. Depending on the composition of the wastes and the combustion conditions, some other compounds, such as oxides of sulphur, oxides of nitrogen and halogens, may be present in the flue gas. When the combustion



products from an incineration process contain these undesirable compounds, a secondary treatment such as scrubbing and/or absorption or filtration is required to lower the concentrations to acceptable levels prior to atmospheric release. R.S. Ottinger et al (1973), (90), lists waste organic streams which may be successfully disposed of by controlled incineration. Among many other compounds, the following ones are included:

Benzene	Methyl chloride
Benzyl Chloride	Methylene chloride
Carbon Tetrachloride	Naphthalene
Chlorobenzene	Perchloroethylene
Chloroform	Styrene
Dichlorobenzene	Tetrachloroethane
Cumene	Toluene
Ethylbenzene	Trichlorobenzene
Ethylchloride	Trichloroethane
Ethylene dichloride	Xylene

Wastes may be classified into two types from a combustion point of view (94):

- combustible liquids
- non-combustible liquids

The first category contains materials having sufficient calorific



value to support combustion. The second category includes materials that do not support combustion (for example water) without the addition of auxiliary fuel.

The wastes should generally have a minimum calorific value of 16.7 to 20.9 MJ/kg to successfully support combustion in air without the assistance of an auxiliary fuel (93). Some authors consider 10.5 to 12.5 MJ/kg as the minimum for properly designed incinerators (38, 43, 98).

As mentioned in Section 10.2.1.4, there are three important parameters which influence complete incineration:

- temperature
- time
- turbulence

Only the temperature may be readily controlled after the incineration unit is constructed. This can be done by varying the air/fuel ratio. A design range of 980 °C to 1090 °C is usually desirable (90, 93).

In general, materials with a low flammability limit, low flash point, and low ignition and autoignition temperatures may be combusted at lower temperatures. The lower temperature limit for direct flame combustion for such compounds is 650 to 760 °C. Once the incineration temperature is determined, the physico-chemical properties of the waste, the residence time and turbulent mixing conditions are considered when an incinerator is selected and designed.

There are a number of different types of incinerators in use (92, 94-98):



Rotary Kiln - Is a slowly rotating cylinder mounted at a slight incline to the horizontal; it is applicable to most organic wastes and well suited for solids and sludges: liquids are fired through auxiliary nozzles; a temperature between 810 °C to 1650 °C is used; residence times are from several seconds to several hours (liquids shorter, solids longer).

Fluidized-Bed - The wastes are injected into a hot agitated bed of inert granular particles, usually sand (1-3 mm diameter); it is suitable for most organic wastes; combustion temperatures up to 870 °C are used; residence times are of the order of seconds for gases and liquids and minutes to hours for solids.

Vortex Incinerator - a high velocity stream jet is supplied tangentially to the waste stream which is injected radially; an air jet atomizes the liquid feed and causes a spiral-flame effect; temperatures up to 1000 °C are used; residence times are from a fraction of a second to one second; the unit is suitable for liquid and dilute sludges.

Cyclone Incinerator - As in the Vortex Incinerator, the air and burning gases follow spiral paths; air is introduced at many points around the circumference of the hearth through inclined tangential high-velocity ports; the unit has similar applications and operating parameters to the Vortex Incinerator.



Sulfonated tars from benzene plants can be successfully incinerated in a fluidized bed incinerator (93). The vortex incinerator is used for disposal of chlorinated hydrocarbon wastes from the manufacture of chlorinated organics (93); unfortunately, no process data are available. A variety of organic chlorides, from aliphatics to PCBs, were successfully destructed in a cement kiln (100) at temperatures of 2500 °C and a residence time of up to 20 seconds. Styrene still residues can be mixed into fuel oil and used in heating furnaces (93). Dichlorobenzene, carbon tetrachloride, chlorobenzene, chloroform, ethyl chloride, ethylene dichloride, tetrachloroethane, perchloroethylene, trichlorobenzene, trichloroethane and trichloroethylene are compounds which should be mixed with another fuel prior to injection into the incinerator. Incomplete combustion may cause formation of phosgene (93).

Secondary Abatement

Many organic wastes cannot be incinerated without some secondary form of treatment. The inorganic content of organic sludges requires the use of a particulate matter removal system. Chlorinated hydrocarbons may produce hydrogen chloride, resulting in emissions of this compound. If there is not sufficient hydrogen in the waste material to accomplish complete conversion of chlorine to hydrogen chloride, chlorine will also be emitted. The hydrogen chloride formed can be removed by scrubbing with water, but carbon tetrachloride, which is relatively insoluble, will pass through the scrubbing system into the atmosphere.

In the absence of an adequate supply of hydrogen, trichloroethylene



is incinerated in accordance with the following reaction:



By the addition of natural gas, all of the chlorine is converted to hydrogen chloride:



In this particular case, natural gas or another auxiliary fuel would be required for complete incineration, because of the low calorific value of trichloroethylene. Usually chlorinated hydrocarbons with less than 60 to 70 % of chlorine support combustion. Hydrogen chloride in the combustion products is neutralized or recovered. Depending on the chlorine content of the incinerated waste material, 15 to 20 % hydrochloric acid can be produced (99). It can be further up-graded to the desired concentration by an extractive distillation process (38, 99). The hydrogen chloride recovery process efficiency exceeds 95 %. J.C. Zimmer and R. Guaitella (38) report tail gas concentrations of hydrogen chloride plus chlorine of no more than 10 ppm.

10.4.2 OTHER METHODS

Other disposal methods include (93):

- dispersal into streams
- lagooning
- deep wells
- land fills

These methods have been used in the past, but are presently considered as being environmentally unsafe for the disposal of



potentially hazardous materials.

Process modification is considered the best method to minimize undesirable emissions, effluent or discharges.



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11 SAMPLING AND ANALYSIS

	SECTION	PAGE NO.
11	SAMPLING AND ANALYSIS	11-1
11.1	SUMMARY	11-3
11.2	INTRODUCTION	11-4
11.3	SAMPLING AND ANALYSIS OF AROMATIC HYDROCARBONS IN OCCUPATIONAL ATMOSPHERES	11-6
11.3.1	Introduction	11-6
11.3.2	Sampling Techniques	11-7
11.3.2.1	Collection in Impingers	11-7
11.3.2.2	Collection in Plastic Bags	11-8
11.3.2.3	Collection by Adsorption	11-9
11.3.3	Analysis Techniques	11-12
11.3.3.1	Indicator Tubes	11-12
11.3.3.2	Colorimetric Techniques	11-13
11.3.3.3	Spectrophotometric Techniques	11-14
11.3.3.4	Gas Chromatographic Techniques	11-15
11.4	SAMPLING AND ANALYSIS OF AROMATIC HYDROCARBONS IN AMBIENT AIR	11-17
11.4.1	Introduction	11-17
11.4.2	Sampling Techniques	11-17
11.4.2.1	Grab Samplers	11-17
11.4.2.2	Cryogenic Collection	11-19
11.4.2.3	Collection by Adsorption	11-19
11.4.2.4	Diffusion Samplers	11-24
11.4.3	Analysis Techniques	11-26
11.4.3.1	Gas Chromatography	11-26
11.4.3.1.1	Sample Introduction	11-26
11.4.3.1.2	Column Technology	11-27
11.4.3.2	Mass Spectrometry	11-30
11.4.3.3	Gas Chromatography/Mass Spectrometry	11-30
11.5	SAMPLING AND ANALYSIS OF AROMATIC HYDROCARBONS AS WATER POLLUTANTS	11-34
11.5.1	Introduction	11-34
11.5.2	Sampling Techniques	11-34
11.5.3	Analysis Techniques	11-36
11.5.3.1	Direct Analysis Techniques	11-36
11.5.3.2	UV Fluorescence Analysis	11-37
11.5.3.3	Gas Chromatographic Analysis	11-37
11.6	REFERENCES	11-39



11.1 SUMMARY

The available literature on the sampling and analysis of selected aromatic hydrocarbons in occupational atmospheres, ambient air, and water has been reviewed and critically evaluated.

Since all of the aromatic hydrocarbons of interest here behave similarly as pollutants, the general approach of this discussion has been to consider these compounds in the class of C_6-C_{10} aromatic hydrocarbons. All of the techniques described have been applied or can be applied to the sampling and analysis of these aromatic hydrocarbons individually or in admixture. The sampling technique of choice for all of the aromatic hydrocarbons of interest is adsorption onto activated charcoal or Tenax GC. The analysis technique of choice is gas chromatography, either used alone for individual compounds or simple mixtures containing these aromatic hydrocarbons, or used in combination with a mass spectrometer, preferably with a dedicated computer, for complex mixtures containing these aromatic hydrocarbons.

Current research efforts in the fields of air and water pollutant analysis, using gas chromatography, point to the need for using glass support-coated capillary columns as this type of column has the resolving power required to separate complex pollutant mixtures into discrete components, for subsequent identification and quantitation.



11.2 INTRODUCTION

Aromatic hydrocarbons are present as pollutants in occupational atmospheres, in ambient air, and in both drinking water and effluent waters.

In the sampling and analysis of any given class of organic compounds, there are two approaches which may be used. The first approach is to sample and analyse a particular environment for members of a class of compounds, such as the aromatic hydrocarbons of interest here, either individually or in simple admixture. The second approach is to sample and analyse a particular environment for all organic pollutants present, including the compounds of interest.

This second approach is the preferred strategy, as, although only certain aromatic hydrocarbons are of interest here, other organic pollutants may also be of concern, either currently or in the future, and there is also the possibility that the detection of certain other pollutants with the aromatic hydrocarbons of interest may give indications of the source of pollution of a particular environment. An example of this would be the presence in ambient air of aliphatic hydrocarbons with the aromatic hydrocarbons, benzene, toluene and xylene, indicating automobile emissions or refinery emissions as the pollution source, depending upon the relative concentrations of the two classes of compounds.

This total pollutant approach necessitates the use of a sampling and analysis technique of very great sensitivity, selectivity and resolution. All of the available sampling and analysis techniques reviewed



here are discussed in light of this requirement.

There may appear to be a contradiction in the techniques described to introduce samples to a gas chromatograph, between occupational air samples and ambient air samples. Solvent desorption followed by solution injection is recommended for introducing occupational air samples to a gas chromatograph, whereas thermal desorption of the whole sample is recommended for ambient air samples. The difference is due to the relative concentrations of pollutants found in each environment. Occupational air pollutants are normally present at the ppm level, and thus, the loss in sensitivity due to using solution injection does not lower sample concentration below the gas chromatograph detection limit, and is offset by the advantages of replicate injections and compound stability using this method. However, ambient air pollutants are often present at the sub-ppb level, and the dilution factor (often 100 times) using solvent desorption and aliquot injection, may be sufficient to reduce pollutant concentrations below the lower detection limits of the gas chromatographic system. Thus thermal desorption of the whole sample to the gas chromatograph is recommended.



11.3 SAMPLING AND ANALYSIS OF AROMATIC HYDROCARBONS
 IN OCCUPATIONAL ATMOSPHERES

11.3.1 INTRODUCTION

Aromatic hydrocarbon vapors are ubiquitous components of the atmospheres in many manufacturing plants. Their use as solvents in degreasing and paint applications and as raw materials and products in industrial processes contribute to this condition.

Semiquantitative vapor concentration measurements have been made for many years utilizing manual sampling pumps and indicator tubes which develop color via a reaction specific to the vapor component. While these methods are useful for general screening purposes, they usually lack the specificity, precision and accuracy necessary to document worker exposure.

Many other methods have been used to determine the concentration of aromatic hydrocarbon vapors in industrial atmospheres. Methods of collection include the use of plastic sampling bags (1-4), absorption in impingers by nitrating solutions (5-7) or organic solvents (8, 9), and adsorption onto silica gel (10-18) or activated charcoal (18-22). Analytical methods have included colorimetry (5-7), infrared (IR) spectrometry (13), ultraviolet (UV) spectrometry (8, 9, 11, 17, 23) and gas chromatography (GC) (15, 18, 24-27).

The most widely accepted method in North America at the present time is sampling by adsorption on activated charcoal, followed by desorption with carbon disulfide and analysis by gas chromatography.



11.3.2 SAMPLING TECHNIQUES

11.3.2.1 COLLECTION IN IMPINGERS

Early methods of sampling aromatic hydrocarbons entailed absorption into impingers containing nitration solutions. Any aromatic hydrocarbons present form dinitro derivatives, and these react, in the presence of carbonyl compounds in alkaline solution, to form colored complexes.

An example of this method is one first reported by Yant and co-workers for the measurement of benzene and toluene (5), using butanone as the complexing agent. Several variations have been described (6, 7), but all of these methods have the disadvantage of not distinguishing between several aromatic hydrocarbons in admixture. These methods are also of low sensitivity (eg 20 μg of benzene 28)).

A method of sampling aromatic hydrocarbons by absorption in a bubbler containing methanol and subsequent determination by UV spectrophotometry has been described by Dambrauskas and Cook (8). This method covers a range of concentrations from 0.02 to 0.48 mg/m^3 for benzene, toluene and xylene. The authors found that the three compounds can be detected down to 5 ppm, but precision is only $\pm 35\%$ for concentrations below 10 ppm. The method also has the disadvantage that the sampling unit requires cooling in dry ice to minimize solvent evaporation.

A further disadvantage to the use of bubbler systems, is that sampling of a breathing zone is difficult with sampling devices containing liquids, particularly if several impingers are required for adequate collection efficiency.



11.3.2.2 COLLECTION IN PLASTIC BAGS

A popular method of sampling and storing atmospheric gases uses flexible plastic bags. However, caution must be used as some substances (eg styrene) in some types of plastic bags can be rapidly lost by diffusion through the bag walls. Thus, the specific conditions of each type of chemical compound in a variety of gas mixtures in a specific plastic bag must be reported.

DeGesero (3) reported the use of Saran bags to routinely sample workers exposed to styrene and ethylbenzene in a polystyrene plant. He reported that the samples must be analysed within 4 hours to prevent loss of styrene.

Baker and Doerr (29) studied the storage of ethylene, 1-pentene, 2-methylpentane, acetone, butyraldehyde and benzene at 30-130 ppm for periods of 16-67 hours in Mylar, aluminized Mylar, Saran, Scotchpak, and aluminized Scotchpak bags. They concluded that these organic gases could be stored satisfactorily in the plastic bags only where the films were impermeable to the studied gases, since diffusion characteristics controlled possible hydrocarbon loss. They recommended that double film bags be used.

Clemons and Altshuller (30) studied systematic changes of hydrocarbon concentrations contained in plastic containers made of Scotchpak and Mylar over a 10 day period. A loss of the major portion of the aromatic hydrocarbons occurred after only a few days of storage. Some of the aromatic hydrocarbons later reappeared in the container. These studies



indicated that long term storage of aromatic hydrocarbons in these containers should be avoided. They also reported that a substance with the same GC retention time as ortho-xylene was very slowly desorbed from the walls of Mylar bags. This materials was interpreted to be an oxygenated component or decomposition product of the plasticizer in the Mylar film.

Altshuller et al (31) found that the stability of aliphatic and aromatic hydrocarbons stored in plastic bags made of Tedlar over 6 hour periods was very good. The concentrations varied by no more than 5 %. However, in a different study (32) a 15 % decrease in the hydrocarbon content of Tedlar bags was measured after several days. The decrease was attributed to wall adsorption and diffusion losses.

11.3.2.3 COLLECTION BY ADSORPTION

Both silica gel and activated carbon have been used as ambient temperature adsorbents of aromatic hydrocarbons in air samples. Van Mourik (12) discussed the use of silica gel as an adsorbent for benzene, toluene, and styrene, plus other organic compounds. He found that the trapping efficiency was adequate except in the presence of large amounts of water vapor (ie when sampling in humid atmospheres). Feldstein et al (13) found the same problem of low retention in the presence of large amounts of water vapor in a study of the use of silica gel to sample air containing aromatic hydrocarbons and halogenated hydrocarbons. Whitman and Johnston (15) demonstrated that water vapor can seriously reduce the efficiency of aromatic hydrocarbon adsorption on silica gel.



To circumvent this problem, they used molecular sieve 5A as a prefilter to adsorb water vapor. One problem with the use of molecular sieves for this purpose is the possible retention of compounds of interest. Desorbing solvents for silica gel samples have included alcohols, dimethylsulfoxide, and carbon disulfide.

Otterson and Guy (19) showed that by using carbon disulfide as a desorbing solvent, activated charcoal could be used to collect atmospheric vapors for analysis by gas chromatography. White et al (20), at the U.S. National Institute for Occupational Safety and Health (NIOSH), chose the charcoal adsorption technique of Otterson and Guy after conducting a literature survey of available sampling and analysis methods for solvent vapors in air. They systematically evaluated collection efficiency, carbon disulfide desorption efficiency, and quantitative determination of 14 solvents using activated charcoal sampling and GC analysis. The sampling and analysis techniques developed by these workers were accepted by the Occupational Safety and Health Administration (OSHA) as standard methods for compliance investigations (33). Trapping efficiencies of activated charcoal for aromatic hydrocarbons were reported to range from 85 % for styrene to over 95 % for toluene and xylenes.

Kupel et al, (34) devised a technique for the identification of individual GC fractions applicable to the complex atmospheres likely to be encountered in plant situations. They utilized a mass spectrometer (MS) to identify GC fractions which were individually collected in



capillary charcoal traps upon elution from the GC.

Because of the low polarity of an activated charcoal surface, organic materials are adsorbed in preference to water and thus water is not as much of a problem here as it is where silica gel is used.

The concentration of aromatic hydrocarbons present in air samples using a cold trap followed by direct injection to a GC is generally accepted as the most sensitive collection technique (35). However, with this method, only one sample is available for analysis. By contrast, the charcoal or silica gel adsorption procedures followed by solvent extraction provides the analyst with the opportunity to aliquot the sample for repeated determinations, allowing replication and confirmation of experimental results. This is particularly important when more than one compound is present in the sample.

The use of activated charcoal tubes to sample occupational atmospheres is now an accepted method in North America (33), and provides adequate sensitivity for the monitoring of aromatic hydrocarbons. However, certain limitations must be considered in the collection of solvent vapors with charcoal tubes:

- a) Charcoal tubes have saturation limits for each compound sampled. When this limit is exceeded, breakthrough occurs.
- b) Vapors collected can be displaced by other vapors which are more strongly adsorbed by the charcoal.
- c) High humidity affects the breakthrough volume of the



charcoal. Breakthrough efficiency must be determined for expected conditions similar to those under which sampling is to be carried out.

- d) Activated charcoal is very prone to artifact formation. The batch of charcoal used to prepare sampling tubes should be evaluated for artifact formation from the compounds of interest.

11.3.3 ANALYSIS TECHNIQUES

11.3.3.1 INDICATOR TUBES

One of the most widely used methods of analysing for aromatic hydrocarbon vapors in industrial atmospheres involves the use of proprietary indicator tubes. Air is drawn through the tube using either a hand pump or small electric pump and the concentration of vapor estimated from the length of a colored zone produced in the tube and the volume of air aspirated. These tubes generally use the reaction of aromatic hydrocarbons with formaldehyde in the presence of sulfuric acid (28). The reagent is impregnated on silica gel.

Benzene and toluene generally give brown colorations, and xylenes and naphthalene give black colorations. These tubes were evaluated for benzene by Ash and Lynch (36) over a concentration range of 20-160 ppm. They found that, in the presence of other hydrocarbons, the tubes were only precise to ± 50 % of the expected benzene concentration at the 95 % confidence level.

Kaljkowski (37) described the use of tubes containing silica gel



impregnated with a solution of 0.7 g/cm^3 of ceric sulfate in fuming sulfuric acid. The tubes were found to be of $\pm 15 \%$ precision for expected levels of benzene at low concentrations and $\pm 5 \%$ precision at high concentrations. Absolute sensitivity to benzene was found to be 0.005 mg/l . However, the tubes are not applicable for estimating benzene exposure in the presence of other aromatic hydrocarbons, particularly toluene and xylene.

Indicator tubes are very useful to identify possible conditions of overexposure to aromatic hydrocarbon vapors. However, because of their lack of specificity, precision and accuracy, their use should always be backed-up by a sampling and analysis method which determines the specific hydrocarbon identities and concentrations accurately, precisely, and quantitatively.

11.3.3.2 COLORIMETRIC TECHNIQUES

Colorimetric methods generally use the reaction of dinitroderivatives of aromatic hydrocarbons with carbonyl compounds in alkaline solution. The reactions produce highly colored complexes, usually blue or violet. A common carbonyl compound used in these methods is butanone (methyl ethyl ketone) (5). The methods, however, are not specific and cannot distinguish several aromatic hydrocarbons in admixture (eg benzene, toluene and ethylbenzene). These interferences can be eliminated adequately only for benzene. Removal relies on oxidation of the alkyl side chains of higher homologues of benzene with chromic acid (28) after nitration, to produce nitroaromatic acids which no longer form the colored complex.



Removal of interferences for determination of higher homologues of benzene is a very tedious procedure and in many cases is incomplete.

Colorimetric methods are also not sensitive enough to determine aromatic hydrocarbons at the ppm level.

11.3.3.3 SPECTROPHOTOMETRIC TECHNIQUES

Infrared spectrophotometers have been used to determine organic vapors in air (13). IR spectrophotometry, however, is of low sensitivity and cannot easily distinguish between different aromatic hydrocarbons in admixture.

UV spectrophotometry has been used by a number of workers. Yamamoto and Cook (23) determined levels of ethylbenzene and styrene in air by UV spectrophotometry. The two compounds were vaporized into an airstream flowing through a midjet bubbler containing isooctane. UV measurements were made at 268 nm (both compounds absorb at this wavelength) and 291 nm (only styrene absorbs at this wavelength). The styrene concentration was estimated by comparison of absorbance measurements against standard solutions of styrene in isooctane measured at 291 nm. This styrene concentration was then used to estimate the styrene contribution to absorbance at 268 nm, with ethylbenzene concentration being obtained by difference. Various mixtures were measured ranging from 10-200 ppm of styrene and ethylbenzene. These workers found that below 25 ppm, the recovery of both substances in the isooctane impinger was greatly reduced. Vapor concentrations of styrene above 25 ppm produced good recovery (greater than 90 %), but



ethylbenzene recovery was poor below 100 ppm. It should be noted that at 268 nm the UV absorbance of styrene is several times greater than that of ethylbenzene. Thus, any inaccuracies in the measurement of styrene concentration at 291 nm are compounded when estimating ethylbenzene concentration by difference from the 268 nm absorbance measurements.

Several other methods using UV spectrophotometric determination of aromatic hydrocarbon concentrations have been described (8, 9, 11, 38). These methods have the basic disadvantage that most of the aromatic hydrocarbons of interest have similar UV absorption spectra. Thus determination of individual aromatic hydrocarbons in mixtures is difficult.

11.3.3.4 GAS CHROMATOGRAPHIC TECHNIQUES

Of the various methods of analysis, GC offers the greatest specificity and sensitivity. Using a flame ionization detector (FID), routine analyses of nanogram levels of aromatic hydrocarbons can be performed. GC is probably the most widely used analytical technique for monitoring aromatic hydrocarbons in industrial atmospheres.

A literature survey carried out by White et al (20) in 1970 found that the GC was most often mentioned as the analytical tool of choice for the determination of organic vapors in industrial atmospheres. They also described a method for sampling and analysing 14 solvents by charcoal adsorption, carbon disulfide desorption, and GC analysis. This method is currently used by NIOSH in compliance investigations (39).



Other analyses using GC techniques have been described (3, 15-19, 22, 24-27, 30, 40), and though some sampling techniques were different the GC analysis method was similar.

The most widely accepted GC column material for aromatic hydrocarbon analysis is a 10 % Carbowax 20M terephthalic acid derivative (commonly called FFAP) on acid-washed, silanized 80/100 mesh Chromosorb W. It should be noted that several stationary phases and supports of similar composition are available from different proprietary suppliers. A 20 ft. x 1/8" stainless steel column is generally used. For mixtures of aromatic hydrocarbons, temperature programming is necessary to separate the higher homologues, but analysis times are rarely longer than 30 minutes when GC conditions are optimized.

The most reliable and reproducible method of introducing samples to the GC is via syringe injection using the solvent flush technique.

GC is the preferred technique for analysing aromatic hydrocarbon vapors in industrial atmospheres because of its superior qualities of selectivity, sensitivity, ease of operation and short analysis time with minimum sample handling required.



11.4 SAMPLING AND ANALYSIS OF AROMATIC HYDROCARBONS IN AMBIENT AIR

11.4.1 INTRODUCTION

In typical ambient atmospheres, vapor-phase organic pollutants are generally present at very low concentrations. The proper evaluation of these organic pollutants depends directly on their collection and transport to the laboratory with a minimum of sample loss or reaction. Because of the very broad range of organic chemical species present in polluted air, and the possibility of reactions or irreversible adsorption, they present many difficult sampling problems.

Many different methods of sampling polluted air have been described. Direct methods of collection include the use of glass bottles (41-44), plastic bags (29, 30, 45, 46), and stainless steel containers (29). Indirect enrichment methods include condensation, absorption with or without chemical reaction (44, 47), and adsorption on various solids (47-55).

The analytical technique of choice which gives the required specificity and selectivity for aromatic hydrocarbon pollutants is gas chromatography. Identification of these components in complex mixtures requires the use of a GC/MS system, preferably with a dedicated computer and appropriate software for data reduction and manipulation.

11.4.2 SAMPLING TECHNIQUES

11.4.2.1 GRAB SAMPLERS

A technique commonly used in air pollution investigations is "grab"



sampling. The procedure is to rapidly acquire a volume of air that can later be analyzed for specific pollutants. The containers are usually made from flexible plastics, metal or glass. Plastic bags have been described earlier (see Section 11.3.2). The main problem with the use of plastic bags is the short amount of time available between sampling and analysis due to possible sample losses from wall adsorption or diffusion through the walls of the bag.

Rigid containers made from stainless steel, glass, etc. can also be used for grab sampling. Pilar and Graydon (44) used 1 litre glass sampling bottles in a survey of the Toronto atmosphere in 1971. 50 ml samples were taken from the bottles using a gas-tight syringe and injected into a cryogenic trap held in a dry-ice-acetone bath. The condensed vapors were subsequently released by heating with a silicon oil bath and analysed by gas chromatography. They found that if samples were taken from the bottles within 4 hours of sampling, wall adsorption losses were minimized. The bottles were stored in the dark before analysis to minimize possible reactions. Precision of analysis was found to be ± 2.5 ppb for a mean 13.4 ppb of benzene (90 % confidence level) and ± 4.1 ppb for a mean 25.0 ppb of toluene.

Stainless steel containers were investigated by Baker and Doerr (29) using atmospheric pressure sampling and sampling under compression up to 1.03 MPa. The containers were found satisfactory for aromatic hydrocarbon analysis but not for oxygenated compounds.

The main limitation to these containers is the small volume of



air that can be sampled. Steel containers have the advantage that air samples can be compressed up to several atmospheres, but wall adsorption effects may still be a problem, particularly during transportation and storage.

11.4.2.2 CRYOGENIC COLLECTION

Cryogenic methods are particularly suitable for analysis of highly volatile substances; however, if liquid nitrogen, oxygen or solid carbon dioxide/acetone is used as a coolant, large quantities of water may accumulate. This can cause a major problem during subsequent chromatographic analysis (55). Drying the air sample by passing it over dessicants prior to cryogenic trapping is not feasible since some compounds of interest may also be removed (56-58). Aerosol formation may also occur with this technique, reducing trapping efficiency.

Simple open-bore, cryogenic traps are now seldom used in air pollution studies (32).

11.4.2.3 COLLECTION BY ADSORPTION

The choice of a technique for concentrating organic vapors from ambient atmospheres depends upon the chemical properties of the constituents of interest. Evaluation of sorbents for a particular air sampling task should be based on the following criteria: quantitative collection efficiencies and recovery of trapped vapors, high breakthrough volumes, minimal decomposition or polymerization of sample constituents during collection and recovery, low background



contribution from the sorbent, and little or no affinity by the sorbent for water (54).

The performance of many sorbents as to their ability to extract and retain organic vapors from a moving air stream have not been adequately studied. The parameters involved in determining the performance of sorbents can be divided into two categories. There are those related to the sampling environment such as flow rate, air temperature, and humidity, and those related to the physicochemical properties of the sorbent such as surface area, particle size, porosity, solute capacity, sorption mechanism, and degree of solute affinity. Also, some of these factors which influence sorbent performance are not independent of each other (54).

Activated carbons have been shown to adsorb aromatic hydrocarbons (59). Where the adsorption is purely physical, the compounds are retained and released without being decomposed. However, one of the problems associated with the use of activated carbon for sampling large volumes of air is the accumulation of significant amounts of water.

A sampling method which is based on gas chromatographic principles employs liquid phases uniformly coated on solid supports. These liquid phases exhibit solution formation with trace organic vapors in the atmosphere at ambient temperatures. Williams has described a collection device for organic compounds, including benzene and toluene, at the sub ppm level. The device consisted of a tube packed with Chromosorb P coated with di-n-butylphthalate (60). During air sampling



the collection tube was cooled in dry ice, and water was removed by using a drying agent prior to drawing the air through the sampler.

Other sorbent materials that have been described are chemically-bonded stationary phases (61, 62) and polymer beads (63-66).

In 1970, Van Wijk (67, 68), described a new type of porous polymer, Tenax GC. This is a polymer of 2,6-diphenyl-paraphenylene oxide and exhibits very high temperature stability. Several applications of Tenax GC have been described (49, 50, 53, 69, 70).

Recently, Pellizzari and co-workers have carried out an extensive characterization study of different sorbents for air sampling (54, 55, 71-74). The sorbents studied were Chromosorb 101, Chromosorb 104, Chromosorb W-HP, Carbowax 400/Poracil C (chemically bonded), oxopropionitrile/Poracil C (chemically bonded), phenylisocyanate/Poracil C (chemically bonded), Porapak Q, activated carbon, Tenax GC and the stationary phases Carbowax 600, dodecylphthalate and tricresyl phosphate coated on Chromosorb W-HP. These workers found that all of these materials, except tricresylphosphate and dodecylphthalate, showed good collection efficiency. However, on carrying out thermal desorption studies they found that all of the sorbents, except Tenax GC and activated carbon, showed high backgrounds of organic compounds which were thermally desorbed (71). These workers then carried out studies on these sorbents for flow characteristics, pressure differential of different particle sizes in a packed bed, and determination of elution and breakthrough volumes for a series of compound classes. From these



and subsequent studies, it was concluded that Tenax GC was the preferred sorbent for use in air pollution studies because of its low affinity for water, high thermal stability, and high breakthrough volume for the greatest number of compounds. The aromatic hydrocarbons of interest all show high breakthrough volumes on Tenax GC, with the possible exception of benzene. Figure 11-1 shows the variation of breakthrough volume of benzene and toluene on Tenax GC over a range of temperatures likely to be encountered when sampling ambient air (73). Breakthrough volume is reported as the volume of air (in litres), aspirated through 2.2 g of Tenax GC, required to produce 50 % breakthrough of the particular compound measured. Breakthrough volumes of the other aromatic hydrocarbons of interest are 3-6 times higher than for toluene (73). It can be seen from Figure 11-1 that some breakthrough of benzene may occur if large volume sampling is carried out at high ambient temperatures, particularly if a sampling cartridge containing less than 2.2 g of Tenax GC is used. In these cases, activated coconut charcoal is used as a back-up to Tenax GC. The significant accumulation of water on activated charcoal is a problem, which can be overcome by desorbing the trapped benzene vapors onto a Tenax GC cartridge with a volume of pure air sufficient to remove the water (water has a breakthrough volume of 0.04 l/2.2 g Tenax GC at 21.1 °C), while not exceeding the breakthrough volume for benzene (73, 75).

Tenax GC, backed up by activated charcoal, is the best adsorbent currently available for air pollution studies. However, because of the low breakthrough volume exhibited by benzene, and generally by C_1 to C_5



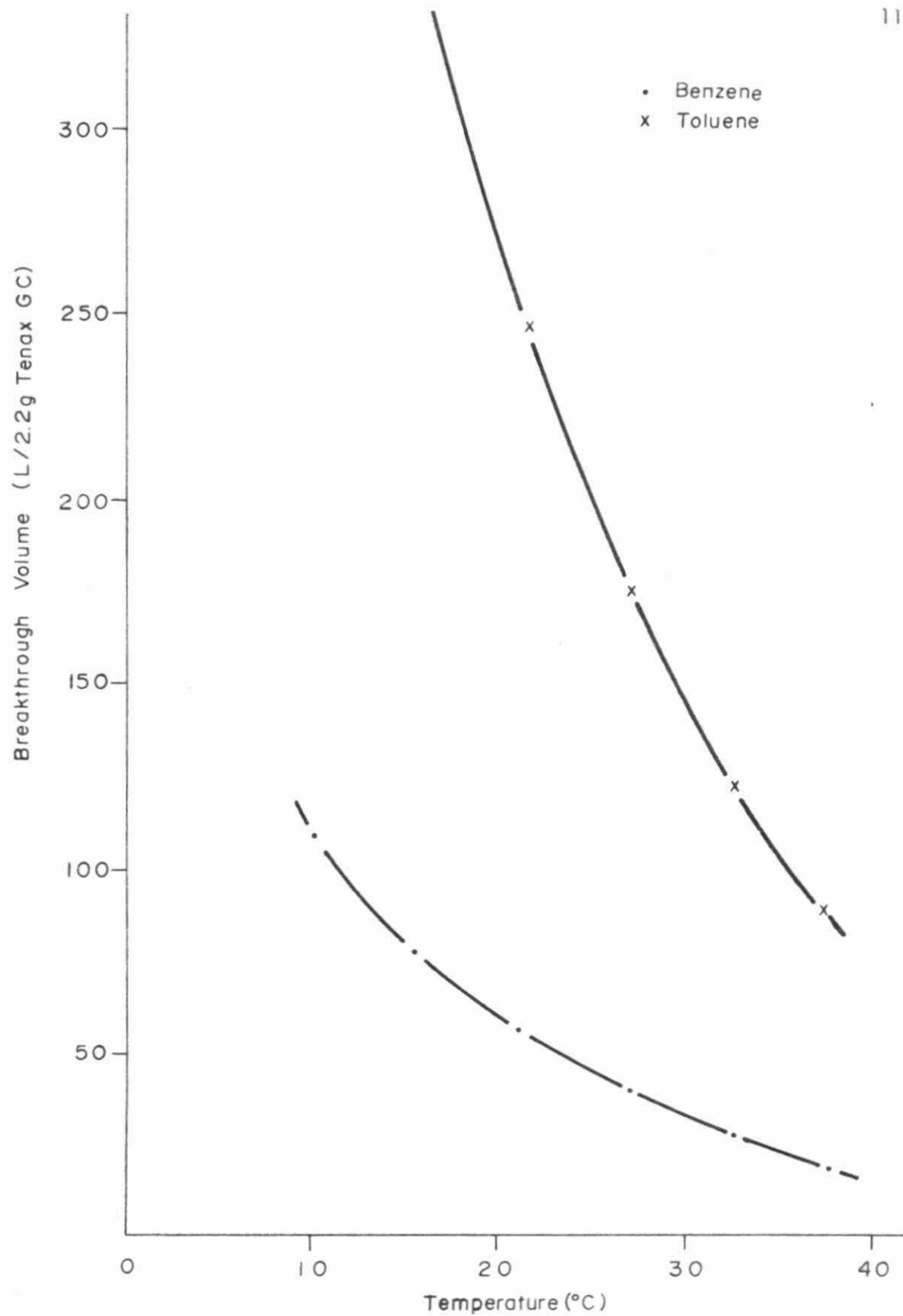


FIGURE 11-1

BREAKTHROUGH VOLUMES FOR BENZENE AND TOLUENE ON
TENAX GC OVER A RANGE OF AMBIENT TEMPERATURES



hydrocarbons, and the undesirable characteristics of activated charcoal (relatively high retention of water and high surface activity which make possible artifact formation an important consideration), a need exists for the development of a complimentary adsorbent to Tenax GC, for sampling low molecular weight hydrocarbons which still retains the desirable characteristics of Tenax GC (75).

A new material recently reported by Union Carbide (76, 77) could be a possible candidate for such a Tenax GC back-up adsorbent. This material is a highly stable polymorph of silica called silicalite, which has a molecular sieve type structure. It is reported to be highly hydrophobic, and the structural voids are large enough to adsorb molecules up to about 0.6 nm diameter. In principle, this includes any molecule the size of benzene or smaller. The material is also reported to be stable up to 1100 °C in air.

Further investigation of this material is necessary to determine its feasibility as a complement to Tenax GC for low molecular weight hydrocarbons such as benzene.

11.4.2.4 DIFFUSION SAMPLERS

A novel approach to sampling for atmospheric pollutants has recently been described by French and Reid (78). This approach is based on establishing a defined diffusion gradient for specific compounds between ambient air and a collection medium impregnated with activated charcoal. The technique described by French and Reid uses a small device (passive dosimeter) whose geometry is such that organic



vapors in the air diffuse through a carefully defined diffusion layer for a known period of time. After sampling is completed, the activated carbon collection element is transferred to a small vial, and the trapped organic vapors are desorbed by an appropriate solvent, normally carbon disulfide. The solution is subsequently analysed by gas chromatography.

The major advantage of using these passive dosimeters is that they are of low cost and do not require the use of mechanical pumps to draw air over the adsorbent to collect organic pollutants. However, these dosimeters are designed for sampling organic vapors at the 10-100 ppm level in occupational environments, and several difficulties arise when applying them to ambient air sampling at the ppb level (78). The dosimeter housing may be a source of contamination from compounds leaching from the plastic materials used in its construction. Also the dosimeter closure method is poor, allowing contaminants to leak into those dosimeters used for blanks. Other difficulties arise mainly from the use of activated charcoal as the adsorbent (high surface activity, batch to batch variation, irreversible adsorption of organic vapors) and from the analysis method used. Solvent desorption methods are inherently less sensitive than thermal desorption directly to the GC (see Section 11.4.3.1.1 below), and impurities in the solvent used can cause serious interferences in the GC analysis.

This method shows great promise as a low cost sampling method for air pollutants. However, the problems associated with the method must first be solved before these passive dosimeters can be applied to systematic air pollution studies.



11.4.3 ANALYSIS TECHNIQUES

11.4.3.1 GAS CHROMATOGRAPHY

For the analysis of organic pollutants in ambient air, gas chromatography is most often used. While there are still many difficulties and limitations to GC analysis, particularly detector sensitivity and column technology, it is the best analysis technique which has the potential to offer the necessary specificity, sensitivity, versatility and speed of analysis to measure trace contaminants that constitute the complex mixture of organic compounds present in polluted air.

11.4.3.1.1 SAMPLE INTRODUCTION

Many different GC analysis methods have been reported. Methods of desorption from sorbents include solvent extraction (79, 80) and thermal desorption directly into the GC inlet (48-50, 54, 60, 62, 65). The use of solvent extraction alleviates problems of artifactual processes associated with thermal desorption, such as pyrolysis, polymerization or incomplete recovery. However, volatile pollutants cannot be quantitatively concentrated from dilute solutions and since GC analysis is limited to small aliquots of liquid samples, only a fraction of the sample can be examined. As a result, overall sensitivity using a solvent extraction method is reduced.

Despite the large concentration effect for organic vapors using adsorption sampling methods, only trace quantities of these compounds are accumulated; thus it is often necessary for the entire sample to be



submitted for analysis (54). Thermal desorption is the most popular method of transferring the entire amount of trapped vapors to the analytical system (48-50, 54, 60, 62, 65, 75). The method used by Pellizzari et al, (54, 55, 71-75) is fairly typical, but includes some interesting design features. The apparatus consists of an aluminium heating block in which a Tenax GC sample cartridge is sealed during desorption. The collected pollutant vapors are purged from the heated cartridge into a gold-plate nickel capillary trap held, typically, at liquid nitrogen temperatures. The trap is designed to allow a thermal gradient to develop between the top and bottom of the trap. This feature essentially eliminates aerosol formation during condensation. After the sample is condensed in the trap, it is transferred to the GC by flash heating and purging with carrier gas. As heating commences from the top of the trap, a thermal gradient is again established which acts to concentrate the sample vapors into a narrow plug as they enter the GC column (75).

11.4.3.1.2 COLUMN TECHNOLOGY

A wide variety of column types and packings are now used in the separation and identification of complex mixtures of organic materials. These column types include conventional packed columns, open tubular capillary columns, support-coated capillary columns, and packed capillary columns. However, gas chromatographic analyses of the hydrocarbon contaminants in polluted atmospheres have, until recent years, remained almost the exclusive realm of packed columns. These



columns do not all provide sufficient resolution to adequately separate the broad range of components detected in urban atmospheres or to make the highly accurate retention time measurements needed for identification purposes.

Aromatic and aliphatic (C_6 and higher) organic pollutants can be resolved by a diverse selection of column types for their routine analysis. Burghardt and Jeltres (80) have reported analysis of aromatic hydrocarbons using a 3 metre, 1/8 in. OD stainless steel column with a 1 % 1,2,3-tris-(2'-cyanoethoxy)-propane, Fractonitrile III, Merck stationary phase. Kopczynski et al (81) have reported separation of aromatic hydrocarbons on a 300 ft., 0.06 in. ID copper wall-coated open tubular (WCOT) column with m-bis-(m-phenoxy-phenoxy)-benzene and Apiezon L at 70 °C. This large-bore column is tolerant to larger sample loads than the more commonly used 0.01 and 0.02 in. ID capillary WCOT columns. Adequate resolution and sensitivity for the alkylbenzenes associated with air pollution were obtained with this column on a routine analysis basis. Mayrsohn et al (82) have used temperature programming in conjunction with small diameter (0.01 in. ID) WCOT columns to achieve higher resolution of the atmospheric burden of C_2 - C_{10} organic compounds, on a routine basis. However, the restricted sample capacity of the 0.01 in. ID capillary columns limits the sample volume for analysis, and this greatly reduces the sensitivity for analysis.

Rasmussen and Holdren (83) reported using a 200 ft., 0.02 in. ID support-coated open tubular (SCOT) column with an OV-101 substrate



operated in a sub-ambient temperature program mode for routine analysis of C_6-C_{12} aliphatic and aromatic organics at trace (0.01 ppb) background concentrations. The SCOT column was chosen because of its inherently larger sample capacity than 0.01 in. ID capillary columns, its durability, and its high resolution. This column has the advantages characteristic of both the open tubular and packed columns, without the pressure drop of packed columns or the low sample capacity of capillary WCOT columns (84). Pellizzari (74) used glass SCOT columns with OV-101 stationary phase to analyse ambient air samples. The major pollutants identified were aliphatic and aromatic compounds.

The main technological difficulties associated with the use of glass SCOT columns is the achievement of uniform distribution of the liquid phase and support on the column wall and control and measurement of flow rate during analysis (85). However, by careful control and calibration techniques these problems can be overcome (75).

A new type of chromatographic packing material has recently been reported (86-89). This material consists of a tightly bound, ultra thin film, less than 1.5 nm thick and approximately 0.2 weight percent, of liquid phase on a solid support (usually Chromosorb W). This material has highly desirable chromatographic properties; short retention times, high selectivity, low bleed, excellent peak symmetry and good resolution of highly polar compounds (86). Liquid phases reported to form this film are Carbowax 20M, SE-30, AN-60, DEGS and linear polyethylene, using Chromosorb W as solid support (87, 88). A description of these



new materials, including preparation and applications, has been published by Karasek and Hill (89).

11.4.3.2 MASS SPECTROMETRY

Mass spectrometry coupled with appropriate auxiliary techniques (such as GC, computer-assisted data processing, and specific ion detection) has the potential to be used to advantage in determining the various relevant organic air pollutants present in the nanogram to picogram range. It has a relatively uniform high sensitivity for all chemical species that can be volatilized, excellent selectivity from interfering materials by use of specific ion detection or high resolution, and it can be used to identify unexpected compounds easily.

High resolution mass spectroscopy (HRMS) has been used by Crittenden and co-workers (65, 90) to analyse air pollutants without GC separation. The major effort of the research was the development of a sophisticated computer program for identifying the inorganic and organic constituents in airborne particulates. However, these workers were able to introduce, directly into the mass spectrometer, gaseous pollutants collected on Chromosorb 102 and desorbed by a thermal-vacuum technique. They found the technique useful for characterizing the organic fraction of polluted air. However, unambiguous identification of specific compounds was seldom possible without the use of a data from other techniques.

11.4.3.3 GAS CHROMATOGRAPHY/MASS SPECTROMETRY

GC-MS is presently a widely used and powerful tool for organic



analysis. Interfacing of the GC-MS system with a dedicated mini-computer, and a variety of output devices such as a CRT, teletype, or XY plotter, and a high speed line printer has become a necessity and common practice.

Mass spectra may be obtained by electron impact ionization (EI) or by chemical ionization (CI). In the latter mode, sample ionization is accomplished by means of an ionized reagent gas. In GC-CI-MS analysis, the reagent gas, such as methane or isobutane, may be introduced through its use as the GC carrier gas with no molecular separator being used at the interface between the GC and MS. The MS ionization source pressure with CI using methane, for example, is typically as high as 1-2 torr, and thus a far higher concentration of methane than sample in the source ensures that sample ionization will occur exclusively by collision with ionized methane. CI results in a much different mass spectrum than EI in view of it being a much lower energy process. CI spectra are characterized by less extensive fragmentation of the molecular ion, and the fragmentation which occurs generally proceeds through loss of neutral species and gives appreciably more stable fragments than is the case with EI (91). It is usual to observe a protonated molecular ion in CI, and this is frequently accompanied by two adduct ions at $M+29$ and $M+41$ (for methane CI) caused by the addition of C_2H_5 and C_3H_5 radicals to the molecule in the MS source. Such adduct ions are generally diagnostic for the protonated molecular ion, and thus it is frequently possible to quickly assign a



molecular weight during GC-Cl-MS analysis.

Since Cl analysis is still relatively new, EI, which is well suited to the analysis of complex organic mixtures, maintains a significant advantage. Over the past few years, extensive data files of EI spectra have been built up, many of these giving particular emphasis to toxic and hazardous materials. Spectral matching is a very useful aid to the interpretation of the mass spectrum.

The basic routines available with all commercial mini-computers for GC-MS are RGC (reconstructed gas chromatogram), mass spectra printing, mass chromatograms, and selected ion monitoring.

The normal RGC plot consists of a reconstructed chromatogram which contains ions of all mass numbers, commonly called a "total ion chromatogram". In order to locate the GC peaks for compounds of interest for which mass spectra are known, RGC plots containing prominent ions in the mass spectra of these compounds may be made. The plots are commonly called "mass chromatograms". For example, in the GC-MS analysis of C_6-C_{10} aromatic hydrocarbons, mass chromatograms for the prominent ions at m/e 77, 91 and 105 will quickly pinpoint the presence of these compounds in the chromatogram of a complex mixture.

The normal mass chromatogram is reconstructed by obtaining the ion current for a given ion from each mass scan stored in the computer memory over the entire GC-MS analysis. In a typical 3-second scan (using quadrupole MS), over a mass range of 1-300 amu, the ion current measurement time for the given ion is only about 0.01 s. However, if



the MS is tuned to this particular ion m/e value without scanning, the desired ion is detected continuously throughout the GC-MS analysis. By this technique, called selective ion monitoring (SIM), it is possible to obtain a factor of 10-100 greater sensitivity (92).

Currently available GC-MS-computer systems can monitor several ions simultaneously in this way. It should be noted, however, that information from compounds not responding to this ion is lost. This essentially eliminates the use of this technique in analyses where only one sample is available.



Grob (105) developed a closed loop sparging system, which involved passing the purged head space gas through a micro carbon filter and back through a 5 litre sample. Concentration factors of up to 10^6 were obtained for compounds up to C_{24} . Bellar (96) used a 5 ml sample and the gas sparging technique to trap organics in drinking water on Tenax GC, and subsequently analysed the organics by thermal desorption into a GC. A modification of this technique using a 1 ft. long Dexsil-300 and Tenax GC trap was used by Duholke and Meresz (106) to analyse organic compounds in St. Clair River water.

Sievers and co-workers (107, 108), in an ongoing research program to characterize the organic compounds present in domestic waste waters before and after treatment by chlorination and ozonization, routinely used gas sparging with nitrogen of volatile organics in a 0.5 - 1.5 l sample of water onto 60/80 mesh Tenax GC. The compounds are subsequently thermally desorbed into a GC and analysed by capillary GC-MS-computer.

Although most efforts have been directed towards head space analysis, considerable effort has been expended to develop new methods for directly adsorbing the organics from water. Burnham and co-workers have used Amberlite XAD resins for this purpose (109, 110). These researchers and Glaze (111) have made extensive use of Amberlite XAD-2 resin for the analysis of organic compounds in drinking water.

11.5.3 ANALYSIS TECHNIQUES

11.5.3.1 DIRECT ANALYSIS TECHNIQUES

A number of researchers have reported success in direct analysis



of polluted water. The use of laser Raman spectroscopy for detection and identification of down to 20 ppm of benzene in water has been described (100, 101). This technique was investigated because of the advantages that no sample preparation is necessary and the system is portable. Application of this technique is, however, limited because of its low sensitivity and single component detection.

A continuous flow instrument, based upon the UV absorption of the aqueous solution (112), has been devised for the determination of trace amounts of organic compounds in chemical plant effluent. The reported sensitivity of the method was 50 ppb for benzene, but it is not specific for aromatic hydrocarbons since many other compounds also absorb UV light.

11.5.3.2 UV FLUORESCENCE ANALYSIS

Schwartz and Wasik (99) reported the use of UV fluorescence spectroscopy to determine benzene, naphthalene and a number of polycyclic aromatic hydrocarbons in water. Problems associated with the measurement of these compounds by this technique in environmental water samples were reported. Suspended matter can increase light scattering and reduce the sensitivity of the method. There is also the possibility of heavy metal ion quenching of the fluorescence intensity. Another problem may be insufficient spectral resolution during the excitation and fluorescence measurements to identify specific constituents in the sample mixture.

11.5.3.3 GAS CHROMATOGRAPHIC ANALYSIS

Direct aqueous injection of samples into the GC has been reported



11.5 SAMPLING AND ANALYSIS OF AROMATIC HYDROCARBONS AS WATER POLLUTANTS

11.5.1 INTRODUCTION

Organic compounds can enter natural waters from a wide variety of sources. Surface waters may be contaminated by organic chemicals discharged in the waste effluents from various industries, run off waters and natural degradation products.

Aromatic hydrocarbons are likely to be present in waters containing effluents discharged from refineries, plastics manufacturers, paint and varnish manufacturers and also where sources of oil and gasoline contamination occur (eg from tankers and freighters on the Great Lakes, from small motor craft, etc.).

Methods of sampling waters for aromatic hydrocarbons have included solvent extraction (93), activated carbon adsorption followed by solvent extraction (94), head-space analysis (95) and inert gas stripping (96, 97).

Methods of analysis include gas chromatography (94-97), UV absorption (93), UV fluorescence (98, 99) and laser Raman spectroscopy (100, 101). The most widely accepted method of analysis is gas chromatography because of its selectivity, sensitivity and ease of operation.

11.5.2 SAMPLING TECHNIQUES

The earliest sampling technique used for organic water pollutants was carbon adsorption. This method involved passing large volumes of



water through a carbon column, drying the carbon, and then extracting it with selected organic solvents, usually chloroform and ethanol. However, this method gives poor recoveries for some organics, and changes in flow rate through the cartridge produce changes in the amounts of organics adsorbed (102).

Liquid-liquid extraction methods using low or high boiling organic solvents followed by GC analyses have been described (103, 104). These methods have provided erratic with low extraction efficiencies for volatile compounds. In addition, large solvent responses and solvent impurities can cause serious chromatographic interferences.

Head space analysis techniques (95) have been employed for a number of years. With this method the sample is sealed in a partially filled container. Each volatile organic compound establishes an equilibrium between the gaseous and aqueous phase. At low concentrations, the ratio of the concentration in the gaseous phase to the concentration in the aqueous phase is a constant (partition coefficient) and is unique for each compound. By analysing the gaseous phase and applying the appropriate partition coefficient, the concentration can be calculated for each organic originally present in the aqueous phase.

A modification of this technique is inert gas stripping. An inert gas is bubbled through the sample and the volatile organics are quantitatively transferred to the gaseous phase. These organics can then be concentrated for GC analysis by adsorption trapping and thermal desorption to a GC. In this manner an analysis performed on the gas phase would have a direct relationship to the aqueous phase concentration.



(106, 113, 114). Although these methods are generally useful for analysis of industrial effluents, the sensitivity is fairly low (around 100 $\mu\text{g/l}$).

Analysis by GC of concentrated samples has been confined to the use of conventional packed columns. The use of GC-MS-computer techniques is necessary for complex mixtures of aromatic hydrocarbons. Such analyses have been reported by several investigators (93, 96, 104-106).

Sievers and co-workers (107, 108, 115, 116) use glass capillary columns and Aue packings (86-88, 116, 117) to routinely analyse volatile organics in domestic wastewaters. Excellent separations are achieved, and mass spectra free of peak overlap and extraneous peaks from column bleed are obtained by a computer enhancement method devised by Biller and Biemann (118). Quantitative data are lost by this method (107), but good mass spectra for qualitative identification and analysis are obtained.

Jones et al (119) have reported a comprehensive analysis scheme for organic materials in process streams. The techniques utilized are liquid chromatography, HRMS, IR spectrophotometry, nuclear magnetic resonance spectroscopy, high performance liquid chromatography (HPLC), and GC-MS. Such a unified approach to the analysis of polluted waters is necessary to obtain all possible data on the compounds present. However, a considerable investment of expertise and instrumentation is required, which restricts the use of this approach to a few specialized laboratories.



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12 ENVIRONMENTAL PERSISTENCE AND FATE



	SECTION	PAGE NO.
12	ENVIRONMENTAL PERSISTENCE AND FATE	12-1
12.1	SUMMARY	12-3
12.2	INTRODUCTION	12-8
12.3	AROMATIC COMPOUNDS IN AIR	12-10
12.3.1	Atmospheric Transport and Transformations	12-10
12.3.2	Reactivity Scales	12-23
12.3.2.1	Scales Based on Reactions with Hydroxyl Radicals..	12-25
12.3.2.2	Scales Based on Hydrocarbon Consumption	12-29
12.3.2.3	Scales Based on NO Oxidation	12-29
12.3.2.4	Scales Based on Oxidant Formation	12-32
12.3.2.5	Scales Based on Eye Irritation	12-44
12.3.2.6	Application of Reactivity Scales	12-45
12.3.3	Measured Ambient Air Concentrations	12-48
12.4	AROMATIC COMPOUNDS IN WATER	12-52
12.4.1	Aqueous Transport, Transformation and Removal	12-52
12.4.2	Measured Concentration in Water	12-55
12.5	REFERENCES	12-66



12.1 SUMMARY

The environmental fate of any substance depends on the medium in which it accumulates, and on the relative efficiencies of the various degradation pathways possible. For the compounds considered here the main degradation pathway is probably atmospheric photooxidation.

Studies have shown that, where these compounds are emitted in aqueous discharges, the half lives for evaporation are short. The actual half life depends, among other considerations, on the degree of turbulence in the aqueous phase. In any case, it does not exceed about seven hours.

With the possible exception of naphthalene, there does not appear to be any significant accumulation of these compounds in sediments. Biological degradation of aromatic compounds can take place, but this is a slow process and does not compete with evaporation. Also, with the possible exception of styrene, hydrolysis and oxidation reactions do not take place at significant rates in the aqueous phase.

Atmospheric degradation of aromatic compounds takes place via photooxidation in the well known photochemical smogs. However, details of reaction mechanisms and products are not well understood. Photochemical smogs form when hydrocarbons and nitrogen oxides are mixed in ambient air and subjected to sunlight. Intensive studies of these reactions have been carried out by a large number of research groups for several years, both in laboratory simulations, and in the ambient atmosphere. The chemistry alone is complex and requires consideration of hundreds of



reactions, but in order to develop a reliable predictive model, meteorological parameters must also be taken into account. Numerous mathematical models have been developed to relate pollutant emissions to ambient air quality through theoretical treatments of the chemical and physical processes taking place. Due to the dearth of information on the atmospheric chemistry of aromatic hydrocarbons, these compounds have not been included in mathematical models to date.

Much of the chemical information for models has been obtained from laboratory experiments mainly based on smog chamber data using rather simple analogues to the complex atmospheric mixtures. A considerable amount of effort has been devoted to the more highly reactive hydrocarbons, such as internally double bonded olefins. Only a very few experiments using aromatic hydrocarbons have been reported. This is at least partly due to the difficulty in carrying out the long chamber experiments required for slower reacting hydrocarbons. An eight hour experiment is suitable for the more reactive hydrocarbons but much longer periods are needed when studying many aromatic compounds. This leads to problems related to trace impurities and wall effects.

Despite these difficulties, some studies have been reported which classify the potential of various aromatic hydrocarbons in forming ozone, and in oxidizing NO to NO_2 . Aromatics are known to produce aerosols when photooxidized, although the carbon balance in smog chamber studies is generally poor, presumably due to aerosol loss at the reaction vessel walls. Recent smog chamber studies of toluene have



resulted in good carbon balances, and it may be significant that one of the major products are methyl phenols (cresols), which are known to be highly toxic.

A number of reactivity scales have been proposed in order to classify various hydrocarbons in terms of their participation in photochemical smog. Several criteria have been used, and include scales based on:

- hydrocarbon reaction rate with OH radicals
- rate of hydrocarbon consumption
- rate of NO oxidation
- rate of oxidant formation
- degree of eye irritation

With the exception of reactivity scales based on eye irritation, the scales mentioned above show much the same general structure, although they do vary in details. The general order of reactivity is listed below in order of increasing reactivity:

- benzene
- chlorobenzene
- dichlorobenzene
- naphthalene
- toluene
- ethyl benzene
- cumene
- xylenes
- styrene



Those compounds less reactive than ethylbenzene may generally be considered to have half lives in excess of one day. Benzene itself is the least reactive, with an expected half life of several days. It is, however, more reactive than are the chlorinated methanes, chlorinated ethanes, or ethane itself. Although no data are available, styrene is expected to be highly reactive with a half life of only a few hours at most.

With regard to eye irritation, those compounds which are precursors to the potent eye irritants such as formaldehyde, acrolein, and especially peroxybenzoyl nitrate (PBN), will appear highest on the list. Thus, styrene and alkyl benzenes, which can form PBN, are high in reactivity with regard to eye irritation.

There are very few reported ambient measurements of aromatics. In Toronto, ambient air levels of benzene and toluene have been reported as an average of 13 and 30 ppb respectively, with a maximum of 98 and 188 ppb. These levels were associated with automobile traffic. Actual concentrations observed vary widely with site and time of day. Reports for a number of urban and industrial areas indicate the average concentration for benzene, toluene, ethylbenzene and the xylenes ranges from about 3 ppb up to 50 ppb. Chlorobenzenes have been observed but at concentrations less than 1 ppb.

These compounds are generally not detectable in aqueous samples except at industrial effluent outflow sites where concentrations may reach several hundred ppm. They are, however, rapidly lost downstream from the source.



There have been some cases where aromatics were found at the ppt level in finished drinking waters in Ontario. The source was attributed to contamination of the anthracite filter medium caused by occasional relatively high levels of aromatics in the raw water entering the treatment plant.



12.2 INTRODUCTION

This chapter deals with, and evaluates, the various degradation pathways for the compounds of interest:

- benzene
- toluene
- xylenes
- ethylbenzene
- cumene
- styrene
- naphthalene

In evaluating the environmental persistence and fate of a compound, it is necessary to determine the possible chemical and physical transformations which can occur, and to identify the relative importance of these transformations for each media within which the compound of interest may be found (eg air, water, soil, etc.). This data must then be combined with information on how readily the compounds are transferred from one medium to another in the environment, and where they are most likely to accumulate. Often, there are insufficient data from which all required parameters may be determined. Therefore, estimates and comparisons with similar compounds are frequently required. Environmental monitoring is essential to verify models, and provide information from which transport and transformation data may be derived.



In this chapter, the aromatic hydrocarbons listed above are considered together, since they behave in a similar manner in the environment. Transport, transformations and measured ambient concentrations are considered both for air and water.



12.3 AROMATIC COMPOUNDS IN AIR

12.3.1 ATMOSPHERIC TRANSPORT AND TRANSFORMATIONS

General Considerations

Hydrocarbons emitted into the atmosphere are subject to transport, dispersion, transformation and deposition via complex physical and chemical processes. The atmosphere must be considered as a dynamic reactor in which the governing factors are constantly changing.

Important meteorological conditions include such parameters as wind speed, mixing height, temperature, relative humidity, turbulence intensity, atmospheric stability and solar intensity. Ground surface characteristics in conjunction with meteorological conditions affect the deposition rate to the earth for various pollutants.

Fresh emissions of hydrocarbons and other species in the atmosphere are constantly changing in amount and character following the cyclic nature of anthropogenic activities. The chemical and physical transformations of these compounds are affected by meteorological conditions.

The prime manifestation of hydrocarbon emissions to the atmosphere (along with NO_x) is the formation of the well known "photochemical smog". It is an interesting paradox that, starting with contaminants that are recognized reducing agents such as NO , and SO_2 , and with hydrocarbons which have no oxidizing power, the end result of sunlight is the production of a powerful oxidant smog with oxidizing agents such as peroxyacyl nitrates and ozone, etc.

Air Quality Simulation

Numerous mathematical models have been developed to relate pollutant



emissions to ambient air quality through theoretical treatments of the chemical and physical processes taking place in the polluted atmosphere: Eschenroeder et al, 1972 (1), Demerjian et al, 1974, 1976, 1977 (2, 3, 4), Reynolds et al, 1974 (5), Niki et al, 1972 (6), Hecht et al, 1972 (7), and others.

Such air quality simulation models find application in:

- indicating areas where further research is needed
- development of environmental legislation
- development of implementation planning
- impact assessment
- source identification
- monitor siting
- transportation and land use planning
- episode control systems

The models vary in their complexity from relatively simple ones, in which only a limited number of chemical reactions are considered in static systems, or where only first order chemical processes are considered along with simple diffusion models, to the complex models involving dynamic systems incorporating time dependent emissions and solar radiation flux, hundreds of chemical reactions and detailed dispersion calculations. The complex models require large computers to handle the required calculations.

Most of the information available today, related to the chemistry of the polluted atmosphere, is derived from laboratory experiments and smog chamber studies using rather simple analogues to the complex atmospheric



mixtures. At the present time, our understanding of the reaction mechanisms in rather simple static systems (eg C_2H_6 , and NO in air irradiated in a smog chamber over 6 to 8 hours) is quite good. Experimental data and computer generated concentration profiles are in good agreement (Figure 12-1).

Even with a "simple" system such as propylene photooxidation a large number of reactions must be considered. Hecht et al, 1972 (7) have had success describing this system using a mechanism comprised of 81 reactions:

- a) 19 reactions on the $NO-NO_2-O_2-CO-H_2O$ system
- b) 19 reactions for the oxidation of propylene by O and O_3
- c) 16 reactions for attack on propylene by OH
- d) 13 reactions for formation and destruction of peroxy nitrates
- e) 8 reactions for decomposition of aldehydes
- f) 6 additional reactions involving free radicals

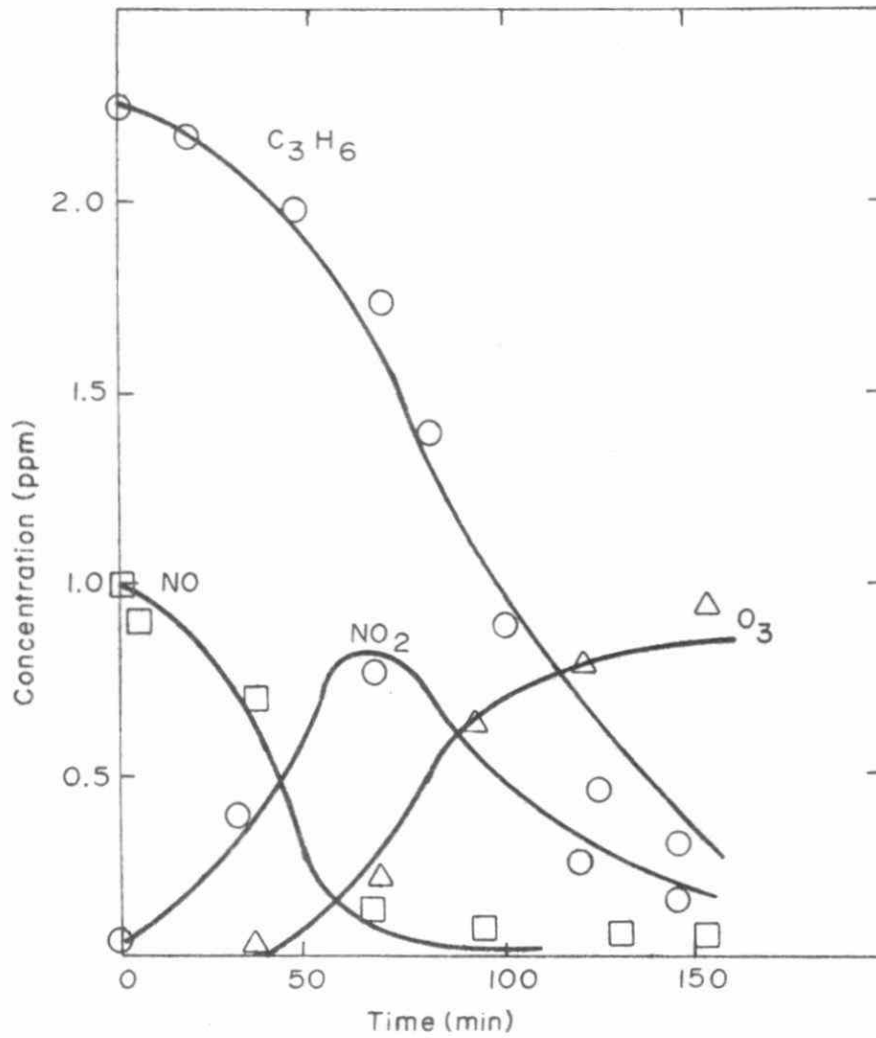
In a very detailed review, Demerjian et al, 1974 (2) list over 450 reactions and rate constants thought to be important in atmospheric chemistry. No aromatic compounds were considered. The complexity of atmospheric photochemical reaction systems stems partly from the multiplicity of organic pollutant species, partly from the large numbers of possible elementary reactions and partly from the difficulties of observation and analysis of components, products and intermediate compounds at the very low concentrations encountered.

Despite these difficulties, there is a reasonable degree of qualitative agreement between air quality simulations and observed diurnal variations



FIGURE 12-1

CONCENTRATION CHANGES ON IRRADIATION OF A
MIXTURE OF ($\text{NO} + \text{NO}_2 + \text{C}_3\text{H}_6$)



Solid line - calculated
Points - experimental data
(Niki et al, 1972 (6))

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- e) 8 reactions for decomposition of aldehydes
- f) 6 additional reactions involving free radicals

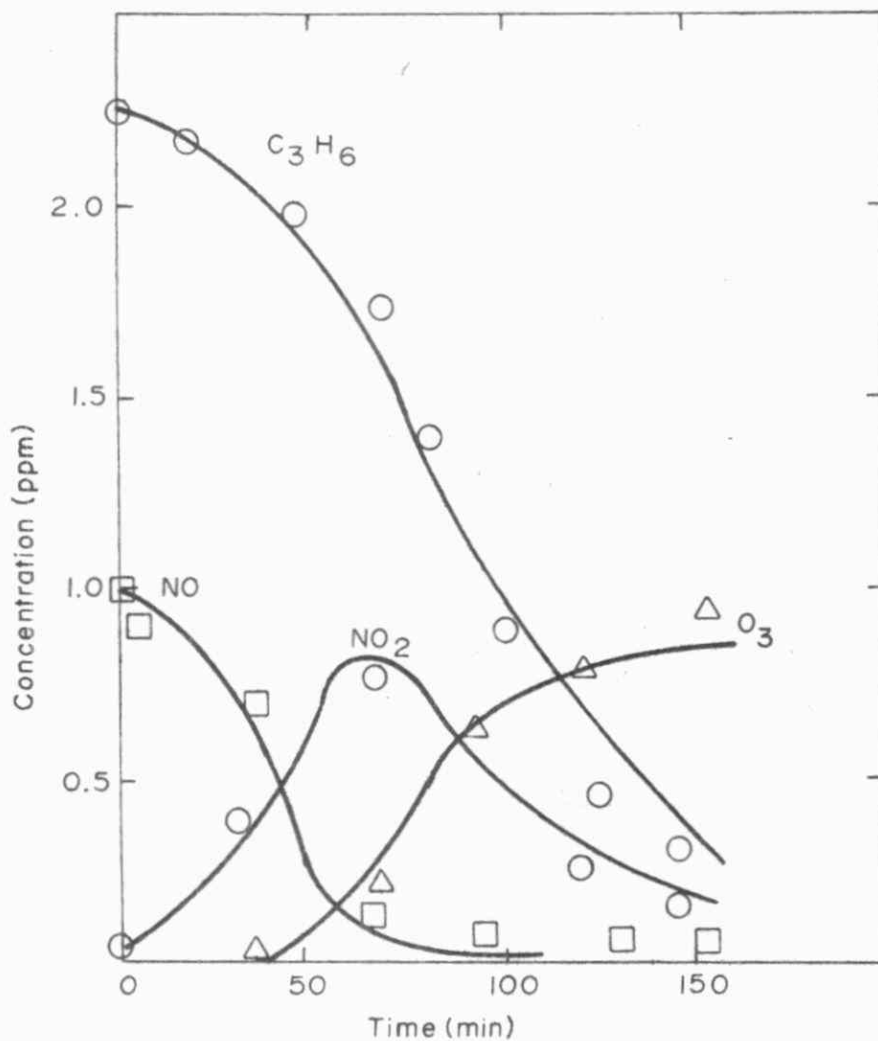
In a very detailed review, Demerjian et al, 1974 (2) list over 450 reactions and rate constants thought to be important in atmospheric chemistry. No aromatic compounds were considered. The complexity of atmospheric photochemical reaction systems stems partly from the multiplicity of organic pollutant species, partly from the large numbers of possible elementary reactions and partly from the difficulties of observation and analysis of components, products and intermediate compounds at the very low concentrations encountered.

Despite these difficulties, there is a reasonable degree of qualitative agreement between air quality simulations and observed diurnal variations



FIGURE 12-1

CONCENTRATION CHANGES ON IRRADIATION OF A
MIXTURE OF ($\text{NO} + \text{NO}_2 + \text{C}_3\text{H}_6$)



Solid line - calculated
Points - experimental data
(Niki et al, 1972 (6))



of the major components of photochemical smog. Studies following reactions in well defined air parcels have been reported by Calvert, 1976 (8), Westberg et al, 1974 (9) and Polgar et al, 1976 (10). Generally, good qualitative agreement with simulations is confirmed although further work is needed for hydrocarbons of low reactivity. These include many of the chlorinated hydrocarbons, light paraffins and aromatics.

A considerable amount of effort has been devoted to studies of highly reactive hydrocarbons such as internally double bonded olefins, but very little to the less reactive compounds. However, consideration of less reactive compounds is now thought to be important because:

- long-range transport of O_3 and its precursors may be responsible for elevated rural concentrations of O_3
- serious pollution episodes have resulted from the occurrence of meteorological conditions which lead to multi-day stagnant air conditions (and persistent high O_3 levels) in which ambient air contains not only each day's fresh pollutant burden but also "aged smog" carryover from the previous days.

Under these conditions a number of compounds previously cited as non-reactive such as benzene, propane, n-butane, etc. can react to produce substantial amounts of O_3 .

General Chemistry of Hydrocarbon/ NO_x Systems

In mixtures of hydrocarbons, NO and clean air, NO_2 will slowly form by:



Once a small amount of NO_2 is present it can absorb light and dissociate:

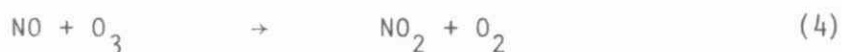


Since O_2 is present in relatively large concentrations in air, O_3 formation is the predominant reaction of O atoms formed in (2):



(M refers to any deactivating third body)

Ozone will rapidly react with NO to form NO_2 again:



Reactions (2)-(4) produce no net change. However, as long as the irradiation is maintained the system must contain a small steady state concentration of O_3 and O atoms.

Occasionally O_3 or O atoms will react with hydrocarbons present to form organic free radicals. These free radicals rapidly combine with O_2 forming peroxyhydrocarbons which can react with other hydrocarbons or NO. The result of these secondary free radical reactions is the formation of compounds such as aldehydes; ketones; alkyl, acyl and peroxyacyl nitrates; hydrogen peroxide; organic peroxides; nitrous, and nitric acids. These secondary compounds can absorb light and dissociate forming more free radicals which then react further.

The net result is the generation of a large number of secondary products and radicals from chain reactions involving free radical mechanisms. Some of these secondary products may have significant inhalation toxicity to man. Other effects such as visibility reduction, materials damage, etc. may also be important.



The identity of the intermediate species which propagate the chains is a subject of much interest as well as theoretical importance. These intermediates may be viewed as providing the "driving force" for the photo-oxidation of hydrocarbons and thus for the development of photochemical smog. At present the OH radical is believed to be the most important intermediate assigned this role during at least the early stages of photochemical smog formation (11, 2, 6, 12).

In urban areas where photochemical smogs are prevalent the following sequence of events, on a diurnal cycle, is commonly observed.

Predawn Hours

- urban activity and emissions at a minimum, primary air contaminants are carbon monoxide, nitric oxide and hydrocarbons
- secondary contaminants such as O_3 , NO_2 , etc. remain at low levels in the absence of photochemical reactions

Sunrise

- increasing activity (eg traffic, etc.) increases the accumulation of primary air contaminants
- not much photochemical activity until the sun is fairly high

Two Hours After Sunrise

- daily injection of NO and hydrocarbons from motor traffic is well under way
- NO_2 and some secondary products such as aldehydes and ketones start to appear



Four Hours After Sunrise

- NO has been reduced to a low level, as it has been converted to NO₂
- NO₂ has reached a peak value
- other secondary products such as aldehydes and ketones, etc. continue to increase
- hydrocarbons have peaked and are starting to decrease
- ozone has just begun to appear
- the appearance of O₃ coincides with the disappearance of NO

Early Afternoon Hours

- O₃ reaches a maximum and begins to slowly decline
- as O₃ built to its peak, NO₂ decreased to a low level
- some of the earlier formed secondary products begin to decline (eg aldehydes)
- hydrocarbons continue to decline

Late Afternoon Hours

- afternoon injection of NO from traffic scavenges the remaining traces of O₃
- hydrocarbons continue to decline to low levels
- NO and NO₂ are both present at fairly low levels

Smog Chamber Studies

The general diurnal cycle described above has been reproduced in smog chamber experiments. At the present time little is known of the mechanisms and significance of photochemical reactions in aged smogs during multi-day



exposures, especially where slower reacting hydrocarbons such as acetylene, ethane, and benzene, etc. are present. Smog chamber experiments are difficult to carry out over more than 6-8 hours due to wall effects.

Since photochemical smog is generated by chain reactions involving free radicals, studies have been made on the effect of various inhibitors to this mechanism which could perhaps reduce the maximum levels of oxidants formed: Gitchell et al, 1974 (13, 14), Spicer et al, 1974 (15). Aniline and diethylhydroxylamine (DEHA) were found, from smog chamber studies, to cause a significant delay in the conversion of NO to NO₂. Aniline and to a lesser extent benzaldehyde and naphthalene decreased the maximum concentration of O₃ formed. However, at least aniline, benzaldehyde and naphthalene lead to significant aerosol formations.

Extrapolation of these results to real atmospheres must be done with care. The delay in photochemical smog formation may merely transfer the oxidant problem from urban to rural areas. Also the structural similarity of DEHA to the carcinogen, diethylnitrosamine, and the lack of knowledge regarding the health effects of DEHA or its oxidation products requires serious consideration be given to its use before exposure to the general public.

At the present time, the mechanisms of oxidation of aromatics in the atmosphere are not known. Very little is known of the major reaction products and consequently aromatics have usually been entirely omitted from computer simulations of photochemical smog formation. Demerjian et al, 1974 (2) have stated that in their models the effects of the addition of



aromatic hydrocarbons are not considered since there are no meaningful experimental data relating to the decay paths of these compounds.

Aromatics are known to produce aerosols when photo-oxidized in the presence of NO_x ; however, the carbon balance in smog chamber studies is generally poor, presumably due to aerosol loss at the reaction vessel walls (16, 17). Miller et al, 1975 (18) studied aerosol formation from exhaust hydrocarbons of automotive engines in smog chamber work using light scattering detection techniques. They concluded that a significant correlation exists between the fuel percent aromatic content and secondary aerosol formation. Also they feel their data indicate that a substantial reduction in aerosol derived photochemically from automobile exhaust can only be achieved with reasonable certainty by reducing the aromatic content of the exhaust to a very low concentration.

While reaction mechanisms and products formed by aromatics in photochemical smogs are not well known, a number of studies have been carried out to determine the potential of aromatics to form O_3 , and oxidize NO to NO_2 , etc. Many of these are discussed in Section 12.3.2 as they relate to the use of reactivity scales. Benzene has been generally found to be rather low in reactivity, but reactivity increases as the number of substituents increases.

In their investigation of hydrocarbon reactivity and eye irritation, Heuss et al, 1968 (19) found that chemical measures of reactivity such as O_3 peak concentration, NO oxidation, etc., correlated well with each other but not at all with eye irritation responses. The most potent precursor to



eye irritation was 1,3-butadiene as might be expected since the photo-oxidation products which arise are formaldehyde and acrolein, two potent eye irritants. The next most potent eye irritant precursors were mono-alkylbenzenes. The irritant was identified as peroxybenzoyl nitrate (PBN) and is more than 200 times as strong as formaldehyde towards eye irritation.

In a study of the effects of aromatic and lead content in gasoline on exhaust hydrocarbon reactivity, Heuss et al, 1974 (20) investigated hydrocarbon reactivity in smog chamber experiments based on parameters such as NO oxidation, O_3 formation, and eye irritation. For gasolines of similar content, the presence or absence of tetraethyl lead did not affect photochemical reactivity of the exhaust hydrocarbons. A low aromatic gasoline was studied for exhaust hydrocarbon reactivity with additions of various amounts of the aromatics: benzene, toluene, ethylbenzene, o-xylene, n-propylbenzene, and isopropylbenzene. No effect on reactivity criteria such as ozone, PAN, formaldehyde or NO_2 formation was observed; however, eye irritant reactivity was increased by aromatic addition according to: isopropylbenzene > (o-xylene, n-propylbenzene, ethylbenzene) > toluene > benzene. This was related to the formation of PBN.

It should be noted that the composition of automotive exhaust and gasoline used are not simply related. For example, in a study reported by Ninomiya et al, 1970 (21) test fuels containing only toluene, isooctane and n-heptane were burned and exhaust hydrocarbon analysis showed the presence of benzene, ethylbenzene, styrene, benzaldehyde and toluene.



In a study of the photochemistry of aromatic hydrocarbons in the presence of NO, Nojima et al, 1974 (22) reported that benzene, toluene and xylenes undergo ring cleavage to form glyoxal, methylglyoxal, and dimethylglyoxal. The yields of glyoxals were low and most of the reaction products were in the form of a yellow solid. More recent studies on benzene and toluene, Nojima et al, 1975, 1976 (23, 24), have identified the solid as substituted benzene and toluene compounds where benzene gives:

- nitrobenzene
- o-nitrophenol
- p-nitrophenol
- 2,4-dinitrophenol
- 2,6-dinitrophenol

and toluene gives:

- o-methylphenol (o-cresol)
- m-nitrotoluene
- p-nitrophenol
- 2-methyl-6-nitrophenol
- 3-methyl-4-nitrophenol
- 2-methyl-4-nitrophenol
- 2-methyl-4,6-dinitrophenol

Analysis of rain samples in Japan also showed the presence of:

- p-nitrophenol
- 2-methyl-6-nitrophenol
- 2-methyl-4-nitrophenol



The presence of these substances could be significant since they are known to cause headache, breathing difficulties, vomiting, rise in body temperature, and numbness in the extremities, which are characteristic symptoms of seriously stricken victims of photochemical smog in Japan.

These observations were confirmed by the recent studies of Akimoto et al, 1977 (25) who carried out smog chamber experiments with the toluene- NO_2 - O_3 - N_2 system. Reaction products identified are:

- benzaldehyde
- o-methylphenol (the m- and p-isomers were less than a few percent of the o-isomer)
- benzyl nitrate
- m-nitrotoluene
- various nitromethylphenols

When nitrous acid was added as a source of OH radicals, the yield of m-nitrotoluene increased markedly relative to the methylphenols. This is interpreted to indicate that O atom attack on toluene is the initial important reaction and not OH attack.

In a recent smog chamber study of the toluene/ NO_x system, Spicer et al, 1977 (26) report for the first time a satisfactory product carbon mass balance. The major products found include:

- PAN
- benzaldehyde
- tolualdehyde
- phthalaldehydes



- phenol
- cresols
- benzoyl alcohol
- formaldehyde

From the observed products, it is concluded that the following mechanisms are indicated:

- 1) side chain attack
- 2) ring cleavage
- 3) addition to the ring

12.3.2 REACTIVITY SCALES

The environmentally important aspects of hydrocarbons in the atmosphere (except near sources where high concentrations may be encountered) are not related to their direct effects, but rather to secondary effects resulting from the products of photochemical reactions which occur in the atmosphere.

The manifestation of photochemical activity as the production of so-called "photochemical smog" has been observed in many large metropolitan areas throughout the world. Over the past years, intensive efforts by numerous research groups have lead to considerable progress toward our understanding of the mechanisms and controlling factors in the chemical and physical transformation of hydrocarbons in the atmosphere.

In an effort to classify the effects of various hydrocarbons in the atmosphere, several attempts have been made to use the concept of reactivity scales: Pitts et al, 1977 (27), Dimitriadis et al, 1977 (28), Farley, 1977 (29), Heuss et al, 1968 (19), Bufalini et al, 1976 (30), Miller et al, 1975,



1973 (18, 31), Altshuller et al, 1971 (32) and others. Such scales are, by definition, without units and are often set relative to one hydrocarbon which may arbitrarily be set at unity or some other value.

The concept that different hydrocarbons have differing capacities to produce photochemical oxidant smogs originated some 20 years ago with the classic work of Haagen-Smit and Fox, 1956 (33). Not every hydrocarbon produces the same manifestations such as oxidant formation, eye irritation, visibility reduction, etc. The reason for this is the differences in reactivity and chemical structure.

Although most of the proposed reactivity scales are similar, there are a number of differences in the details, as would be expected since they are based on different criteria.

In the application of reactivity scales to the development of standards, care must be exercised to ensure that the desired reduction in adverse effects will be achieved. This will depend on the criteria for which the reactivity index is based.

Due to the fact that aromatic hydrocarbons are generally less reactive than olefins, they have received much less attention in the literature. However, their importance has recently been considered by many groups, especially as they may be significant contributors to oxidant formation in aged smogs during stagnation episodes or in relation to long range transport. Unfortunately, most smog chamber data are limited to periods of 6 to 8 hours since trace impurities and wall effects are too difficult to eliminate over periods of 2 or more days. It is over this longer time span that the effects of aromatic hydrocarbons could be significant.



12.3.2.1 SCALES BASED ON REACTIONS WITH HYDROXYL RADICALS

The important role of OH in photochemical smog formation is well established on the basis of both experimental and computer modeling studies: Demerjian et al, 1974 (2), Niki et al, 1972 (6), Finlayson et al, 1976 (12) and others. The OH radical has now been studied both in the laboratory and in ambient air: Wang et al, 1975 (34) and Davis et al, 1976 (35).

With chemical kinetic information now available concerning OH radical reactions, a reactivity scale for hydrocarbons has been proposed which is based, not on secondary manifestation criteria, but rather on the primary chemical act of OH radical attack on the organic chemical of interest: Pitts et al, 1976 (36), and Darnall et al, 1976 (37). Since the first step in atmospheric degradation, for most organic chemicals, is attack by OH then the lifetime of the compound of interest, before chemical transformation, is related to the rate at which it reacts with OH, and only those chemicals which undergo such reactions at a significant rate are of consequence with respect to secondary effects.

Thus, such a scale can indicate the potential that various compounds have for the formation of secondary effects. If, however, the criteria being considered is the degree to which secondary effects are manifested, then this reactivity scale is inadequate since a consideration of reaction mechanisms and products beyond the primary step is needed.

Darnall et al, 1976 (37) have chosen to divide the reactivity scale into five classes with each class based on order of magnitude differences



in reactivities of organics toward OH relative to methane which is set at unity. The class divisions are reproduced in Table 12-1 in which half lives are also given based on a constant OH concentration of 10^7 radicals/cm³.

Over 100 compounds have been fitted into the reactivity scale. Those organic compounds of concern to this report and a number of others are listed in Table 12-2 according to the various classes.

Class I is the least reactive; reactivity increases over five orders of magnitude up to Class V. Class I contains methane and most of the halocarbons. Other light halocarbons are found in Class II along with carbon monoxide, ammonia, acetylene and ethane. Almost all alkanes appear in Class III with the more reactive alkenes in Classes IV or V. Oxygenates and aromatics appear in Classes III or IV. It is interesting that most natural occurring hydrocarbons are in the highly reactive Classes IV or V. The highly reactive internally double bonded olefins are in Class V.

Classes I and II contain relatively few compounds compared to Classes III, IV and V. This indicates that most organic compounds will react at significant rates in the atmosphere. This conclusion was also drawn by Altshuller et al, 1971 (32) in their review of the literature. They state that "almost every hydrocarbon, except methane, can produce some oxidant when photo-oxidized in the presence of high enough ratios of hydrocarbons to oxides of nitrogen".



TABLE 12-1
REACTIVITY SCALE FOR ORGANICS BASED ON RATE OF
CONSUMPTION DUE TO REACTION WITH
THE HYDROXYL RADICAL

<u>Class</u>	<u>Half-life^a</u> <u>(days)</u>	<u>Reactivity Relative</u> <u>to Methane (=1)</u>
I	≥ 10	≤ 10
II	1 - 10	10 - 100
III	0.1 - 1	100 - 1000
IV	0.01 - 0.1	1000 - 10,000
V	≤ 0.01	$\geq 10,000$

^a $t_{1/2} = 0.693/k_{OH}[OH]$. $[OH]$ is assumed to be 10^7 radicals/cm³.



TABLE 12-2

REACTIVITY CLASSIFICATION BASED ON REACTION
WITH THE HYDROXYL RADICAL

CLASS I ($<4.8 \times 10^7$) ^a	CLASS II ($4.8 \times 10^7 - 4.8 \times 10^8$) ^a	CLASS III ($4.8 \times 10^8 - 4.8 \times 10^9$) ^a	CLASS IV ($4.8 \times 10^9 - 4.8 \times 10^{10}$) ^a	CLASS V ($>4.8 \times 10^{10}$) ^a
Trifluoromethane 1,1,2-Trichloro-1,2,2-trifluoroethane Tetrafluoromethane 1,2-Dichloro-1,1,2,2-tetrafluoroethane Chlorotrifluoromethane Dichlorodifluoromethane Fluorotrichloromethane 1-Chloro-1,1-difluoroethane Tetrachloromethane Difluoromethane Methane 2-Chloro-1,1,1-trifluoroethane 2-Chloro-1,1,1,2-tetrafluoroethane 1,1,1-Trichloroethane Fluoroethane Dichlorodifluoromethane 2,2-Dichloro-1,1,1-trifluoroethane 1,1-Difluoroethane Chlorodifluoromethane Bromomethane Chloromethane Chlorodifluoromethane	Trichloromethane Dichloromethane Carbon monoxide Ammonia Acetylene 1,2-Dichloroethane 1,2-Dibromoethane Ethane 1,1-Dichloroethane Chloroethane	Neopentane Methanol Methylacetylene 2,2,3,3-Tetramethylbutane Cyclobutane Benzene Isobutane Propane n-Butane Ethanol Methyl ethyl ketone Isopentane 1-Propanol 2,2,4-Trimethylpentane 2,2,3-Trimethylbutane n-Propyl acetate Allene 2,3-Dimethylbutane Hydrogen Sulfide 2-Methylpentane sec-Butyl acetate Toluene Cyclopentane n-Propylbenzene Isopropylbenzene n-Hexane n-Pentane p-Menthane 1-Butanol Cyclohexane 2-Propanol 4-Methyl-2-pentanol 3-Methylpentane Ethene	Ethylbenzene n-Octane Diethyl ether p-Xylene p-Ethyltoluene o-Ethyltoluene o-Xylene Tetrahydrofuran Methyl isobutyl ketone p-Cymene di-n-propyl ether m-Ethyltoluene Methoxybenzene Methylamine m-Xylene 1,2,3-Trimethylbenzene Diisobutyl ketone Propene 3,3-Dimethyl-1-butene 1-Pentene 1-Hexene 1,2,4-Trimethylbenzene Methyl mercaptan o-Cresol 1-Butene 1-Heptene 1,3,5-Trimethylbenzene Isobutene cis-2-Butene 2-Methyl-1-butene α-Pinene cis-2-Pentene β-Pinene trans-2-Butene Cyclohexene 1,3-Butadiene Isoprene	2-Methyl-2-butene 3-Carene 1-Methylcyclohexene 8-Phellandrene Carvomenthene d-Limonene 2,3-Dimethyl-2-butene Dihydromyrcene Myrcene cis-OCimene

^a Range of values (in liter mole⁻¹ sec⁻¹) for the rate constant for reaction of the OH radical with the listed compounds.



12.3.2.2 SCALES BASED ON HYDROCARBON CONSUMPTION

The rates of reaction, or time for partial consumption, of various hydrocarbons have been used to classify reactivities. Altshuller, 1971 (32) has reviewed available data for a number of compounds and ranked their reactivities.

Table 12-3 and 12-4 list reactivities based on an arbitrary scale in which the most reactive compound is rated at 10. These data are based on smog chamber experiments.

It can be seen that branched or straight chained olefins with internal double bonds form the most reactive class.

The tri- and tetraalkylbenzenes and olefins with terminal double bonds (except ethylene) rank next followed by the dialkylbenzenes, aldehydes and ethylene. Toluene is less reactive than ethylene and the paraffinic hydrocarbons, acetylene, and benzene are less reactive than toluene.

12.3.2.3 SCALES BASED ON NO OXIDATION

In the atmosphere during daylight hours there is a rapid equilibrium established between NO_2 , NO and O_3 which results from the reactions:



Although other concurrent reactions are also taking place, reactions 1-3 are rapid by comparison and hence a steady state for O and O_3 may be assumed on a short time scale. This assumption gives:



TABLE 12-3

REACTIVITY CLASSIFICATION BASED ON
HYDROCARBON CONSUMPTION - I

<u>HYDROCARBON</u>	<u>RANKING OF HYDROCARBONS</u>		
	a	b	c
Tetramethylethylene	10	10	10
trans-2-Butene	6		8
cis-3-Hexene		6	
Isobutene	1.5	2	2
1,3-Butadiene	1		
Propylene	1	2	1
m-Xylene		1	
p-Xylene	0.5	0.5	
Ethylene	0.1	0.3	
Hexanes, octanes	<0.1		
Pentanes	<0.01		

a - Schuck et al, 1959 (38)

b - Stevens et al, 1962 (39)

c - Tuesday, 1963 (40)



TABLE 12-4

REACTIVITY CLASSIFICATION BASED ON
HYDROCARBON CONSUMPTION - II

<u>AROMATIC HYDROCARBON</u>	<u>RANKING*</u>
1,2,3,5-Tetramethylbenzene	10
1,3,5-Trimethylbenzene	8
1,2,4-Trimethylbenzene	6
1,2,3-Trimethylbenzene	6
m-Xylene, 3-methylethylbenzene	3
o-Xylene	1.5
p-Xylene, p-diethylbenzene	1.5
Toluene, ethylbenzene, isopropylbenzene	1
Benzene	0.5

* Based on percent consumed in first hour of reaction after Kopczynski, 1964 (17).



$$\frac{d [O]}{dt} = 0 \quad \text{and} \quad \frac{d [O_3]}{dt} = 0$$

which leads to:

$$[O_3] = K \frac{[NO_2]}{[NO]}$$

(where K is a constant)

Thus the amount of O_3 formed is related to the ratio of NO_2 to NO or the amount of NO which is oxidized to NO_2 .

The relative ability of various hydrocarbons to promote the oxidation of NO to NO_2 in smog chamber experiments can thus be used to indicate the potential for O_3 formation.

Reactivity scales based on this have been proposed. Table 12-5 and 12-6 after Altshuller et al, 1971 (32) and Briggs et al, 1977 (41) are estimates from the best available literature data.

Although there are some differences (likely arising from differences in smog chamber conditions used), the ranking of hydrocarbons is similar in both tables.

Benzene is fairly low in reactivity with the alkyl substituted aromatics such as toluene, xylene, and tri- and tetramethylbenzene showing increased reactivities. Methane is low in reactivity and the reactivity of higher alkanes increases with the chain length. Olefins are generally of high reactivity (except ethylene), especially those having internal double bonds.

12.3.2.4 SCALES BASED ON OXIDANT FORMATION

In air pollution studies, the term "oxidant" refers to that group



TABLE 12-5

RELATIVE REACTIVITIES OF HYDROCARBONS BASED
ON ABILITY TO PARTICIPATE IN PHOTOOXIDATION
OF NITRIC OXIDE TO NITROGEN DIOXIDE

HYDROCARBON	RANKING	
	Altshuller et al 1963 (42)	Glasson et al 1965 (43)
2,3-Dimethylbutene-2		10
2-Methyl-2-butene		3
trans-2-Butene	2	2
Isobutene	1	
Propylene	1	0.5
Ethylene	0.4	0.3
1,3,5-Trimethylbenzene	1.2	1.2
m-Xylene	1	0.9
1,2,3,5-Tetramethylbenzene	0.9	0.7
1,2,4-Trimethylbenzene	0.6	0.7
o- and p-Xylene	0.4	0.4
o- and p-Diethylbenzene	0.4	0.4
Propylbenzenes	0.3	0.2
Toluene	0.2	0.2
Benzene	0.15	0.04
n-Nonane	0.15	
3-Methylheptane	0.15	
n-Heptane		0.2
Methylpentanes	<0.1	0.2
Pentanes		0.2
2,2,4-Trimethylpentane	0.15	0.15
Butanes		0.1
Ethane		0.03
Methane		<0.01
Acetylene	0.1	



TABLE 12-6

REACTIVITIES OF AROMATICS, PARAFFINS AND
OLEFINS BASED ON NO OXIDATION*

<u>COMPOUND</u>	<u>RELATIVE REACTIVITY</u>
Aromatics	
Benzene	0.10
Toluene	0.25
p-xylene	0.50
o-xylene	0.50
m-xylene	1.00
Ethylbenzene	0.34
1,3,5-Trimethylbenzene	1.50
1,2,3,4-Tetramethylbenzene	1.00
Paraffins	
Methane	0.10
Propane	0.40
n-Butane	0.75
n-Hexane	0.93
Olefins	
Ethylene	0.50
Propylene	1.00
Isobutene	1.00
Trans-2-butene	3.50

* Propylene arbitrarily set to unity.



of substances capable of oxidizing potassium iodide or other reference chemicals. Therefore, included in this group are ozone, nitrogen dioxide, peroxyacyl type nitrate compounds, hydrogen peroxide and other possible organic oxy and hydroperoxy compounds.

Since the relative responses of various oxidant measurement techniques differ from each other and also for the particular oxidant being determined, data are difficult to compare. Hence hydrocarbon reactivity scales which have been proposed (based on oxidant formation criteria) use ozone specific measurements for a data base. Experimental data are obtained from smog chamber work.

Ozone concentration as a measure of reactivity is very complex since it is dependent on a number of parameters such as initial hydrocarbon to NO_x ratios, and irradiation time, etc. Less reactive hydrocarbons require long irradiation times which are difficult to carry out in smog chamber experiments.

Recently Farley, 1977 (29) has reported a thorough review of oxidant formation data from smog chamber studies over the last ten years. To obtain reactivity classes, all available O_3 maximum concentration data were pooled and normalized to toluene = 1. For the most part, these data involved irradiation of pure compounds in the presence of NO_x at a molar hydrocarbon to NO_x ratio of about 2.

While this ratio may be considered as "typical" for urban atmospheres, considerable variations can be expected. At lower HC-to- NO_x ratios, O_3 formation is inhibited due to reaction with NO . At higher HC-to- NO_x ratios,



Farley concludes that the more reactive hydrocarbons are not markedly affected (especially as they fit into his classification scheme). The less reactive hydrocarbons may be affected to a larger extent. Data of Heuss, 1975 (44) indicate a definite increase in O_3 formation for n-alkanes with HC-to- NO_x ratios increasing from 2 to 6. However, data reported by Altshuller, 1969 (45) shows essentially no increase in O_3 until the HC-to- NO_x ratio reaches ten or higher. Recent airborne studies reported by Westberg et al, 1974 (9), Polgar et al, 1976 (10), and Calvert, 1976 (8) indicate a low reactivity in the atmosphere for light paraffinic hydrocarbons. Thus, caution should be exercised in assigning high or moderate reactivities to paraffinic hydrocarbons based on smog chamber experiments alone.

Table 12-7 summarizes data on some of the compounds as reported by Farley, 1977 (29) divided into five classes of reactivity. Generally, the paraffins show the lowest potential for peak ozone formation, aromatics are intermediate, and olefins show the greatest potential. Alkyl substitution of benzene increases the potential for peak O_3 formation over that for benzene itself.

Dimitriades et al, 1977 (28) propose a reactivity scale divided into two classes - non-reactive and reactive. All hydrocarbons which, under "optimum" irradiation conditions in smog chamber studies, are capable of producing peak O_3 levels of 0.08 ppm or higher are considered to be reactive, while the remainder are listed as non-reactive.

Optimum conditions are identified from smog chamber studies which



TABLE 12-7

HYDROCARBON REACTIVITY CLASSIFICATION BASED ON
MAXIMUM O₃ PRODUCTION - I

<u>HYDROCARBON</u>	<u>RELATIVE REACTIVITY</u> Normalized to Toluene = 1	<u>REACTIVITY CLASS</u>
1,3,5-Trimethylbenzene	2.0	5
Tetramethylethylene	2.0	5
Isobutene	1.8	5
m-Xylene	1.5	4
o-Xylene	1.3	4
Ethylene	1.3	4
p-Xylene	1.1	4
Toluene	1.0	3
Ethylbenzene	0.88	3
Cumene	0.78	3
n-Propylbenzene	0.70	3
Isobutylbenzene	0.57	3
n-Pentane	0.95	2
Cyclohexane	0.59	2
t-Butylbenzene	0.49	2
n-Hexane	0.33	2
Isopentane	0.33	2
Benzene	0.09	1
Propane	0.0	1
Ethane	0.0	1



give, for the selected irradiation time and hydrocarbon to NO_x ratios, the maximum peak O_3 concentrations. This procedure is intended to identify as non-reactive only those compounds which under no circumstances will yield O_3 peak concentrations exceeding 0.08 ppm. Available literature data are used to classify various compounds. However, not all data are for optimum conditions and more studies are needed, especially for the less reactive hydrocarbons.

Table 12-8 lists a number of hydrocarbons rated under this system. The division between reactive and non-reactive falls between ethane and propane. Benzene and the chlorinated hydrocarbons are rated as non-reactive.

In an earlier publication, Dimitriadis, 1974 (46), suggested a five class reactivity scale based on pooled smog chamber data from the Battelle, SRI and Shell smog chambers. The results for each compound studied were normalized to toluene and averaged. The results are listed in Table 12-9.

In this scale benzene is placed in the non-reactive Class I. Mono-alkylbenzenes are in the next reactive Class II while di- and tri-alkyl benzenes are in the highly reactive Classes IV and V respectively. C_1 - C_3 paraffins are in the non-reactive Class I along with perhalogenated compounds while C_{4+} alkanes are in Class III along with styrene. Olefins are in Classes IV and V.

Bufalini et al, 1976 (30), derived a reactivity scale with five classes based mainly on theoretical grounds. Their concept is that O_3 can be considered to be an intermediate (B) of two consecutive reactions:



TABLE 12-8

HYDROCARBON REACTIVITY CLASSIFICATION BASED ON
MAXIMUM O₃ PRODUCTION - II

<u>HYDROCARBON</u>	<u>MAXIMUM O₃</u> (ppm)
Acetonitrile	0
Benzaldehyde	0
1,1,1-trichloroethane	0
Chloroform	0
Benzene	0.02
Methylene chloride	0.03
Ethane	0.03
Propane	0.08
Acetylene	0.10
Isobutyl Acetate	0.18
Acetone	0.18
n-Butane	0.23
Methanol	0.25
Acetic Acid	0.26
t-Butanol	0.28
Methyl ethyl ketone	0.30
Isopropanol	0.32
Acrylonitrile	0.37
Perchloroethylene	0.49



TABLE 12-9

HYDROCARBON REACTIVITIES BASED ON O₃ FORMATION

<u>CLASS I</u> (nonreactive)	<u>CLASS II</u> (reactive)	<u>CLASS III</u> (reactive)	<u>CLASS IV</u> (reactive)	<u>CLASS V</u> (reactive)
C ₁ -C ₃ paraffins	mono-tertiaryalkylbenzenes	C ₄₊ paraffins	primary and secondary -	aliphatic olefins
acetylene	cyclic ketones	cycloparaffins	alkylbenzenes	α-methyl styrene
benzene	tertiary-alkyl acetates	styrene	dialkyl benzenes	aliphatic aldehydes
benzaldehyde	2-nitropropane	n-alkyl ketones	branched alkyl ketones	tri and tetra-alkyl
acetone		primary and secondary -	primary and secondary -	benzenes
methanol		alkyl acetates	alkyl alcohols	unsaturated ketones
tertiary-alkyl alcohols		n,n-dimethyl acetamide	partially halogenated	diacetone alcohol
perhalogenated hydrocarbon		partially halogenated	olefins	ethers
phenyl acetate		paraffins		
methyl benzoate				
ethyl amines				
dimethyl formamide				





The organic compound (A) is assumed to decay only by OH attack. It is assumed that the hydrocarbon is completely oxidized to CO_2 or formic acid, and the oxidation of NO to NO_2 by RO_2 , RCO_3 and HO_2 radicals (formed in the hydrocarbon decay process) always leads to O_3 formation as a result of NO_2 photolysis. These radicals are assumed not to take part in chain terminating reactions.

The decay of O_3 was considered to be pseudo-unimolecular except for the reaction with NO and olefins. The reaction of NO with O_3 is not a degradation path, however, since NO_2 formed will photodecompose to form O_3 again. The reaction of O_3 with olefins was not considered because its contribution is minimal, even for fast reacting olefins like trans-2-butene. A reasonable steady state concentration of OH is assumed.

Following these assumptions, an average ozone concentrations were calculated during reaction of 99 % of the hydrocarbon.

Five reactivity classes were defined over a range of average O_3 concentrations from less than one up to 16 ppm. The results for a number of compounds are presented in Table 12-10. The lower alkanes (methane and ethane) appear along with CO and acetylene in the lowest reactivity class. Ethene is in Class II with higher alkanes. Internally double bonded alkenes and alkyl substituted benzenes appear in the highly reactive Class V.

Included in the calculations of Bufalini et al, 1976 (30) is the time required to reach 99 % decomposition of the hydrocarbon (Table 12-11).



TABLE 12-10

REACTIVITY CLASSIFICATION FOR VARIOUS HYDROCARBONS

BASED ON AVERAGE OZONE CONCENTRATIONS UP TO

99 % OF HYDROCARBON DECOMPOSITION

<u>CLASS I</u>	<u>CLASS II</u>	<u>CLASS III</u>	<u>CLASS IV</u>	<u>CLASS V</u>
1 ppm	1-4 ppm	4-6 ppm	6-8 ppm	8-16 ppm
Carbon monoxide	Formaldehyde	Propionaldehyde	n-Butane	trans-2-Butene
Methane	Acetaldehyde		Propene	m-Xylene
Acetylene	Ethylene		Butyraldehyde	1,2,4-Trimethylbenzene
Ethane			Benzene	Toluene



TABLE 12-11

REACTIVITY PARAMETERS FOR VARIOUS HYDROCARBONS

<u>COMPOUND</u>	<u>TIME FOR 99 % REACTION, MIN.</u>	<u>TIME TO PEAK OZONE VALUE, MIN.</u>
1,2,4-Trimethylbenzene	61.6	48.5
m-Xylene	87.4	63.9
Toluene	492	224.4
Benzene	529	225.4
trans-2-Butene	25.5	26.7
Propene	128.8	91.2
Ethene	602.6	259.5
Acetylene	1.22×10^4	1178.9
n-Butane	768.2	303.4
Ethane	6062	886.2
Methane	2.25×10^5	2777.1
Butyraldehyde	123	88.0
Propionaldehyde	123	88.0
Acetaldehyde	123	88.0
Formaldehyde	128.8	91.2
Carbon monoxide	1.28×10^4	1209.7



The data predict (especially for benzene, toluene, etc.) that high concentrations of ozone could be expected in rural downwind areas away from high emission sources.

Since this reactivity scale is based on the assumption that intermediate hydrocarbon oxidation products are rapidly converted to CO_2 or formic acid by chain reactions, an overestimate of the amount of O_3 generated in the atmosphere may result.

The question of the validity of this assumption is especially open for aromatic hydrocarbons, since a thorough product study has not been made for this class of compounds. Aromatics are known to produce aerosols when photo-oxidized in the presence of NO_x and the carbon balance in smog chamber studies is generally poor, presumably due to aerosol loss at the reaction vessel walls (16, 17). This would lead to an overestimate of O_3 produced by aromatics as the ultimate decay product is not CO_2 .

12.3.2.5 SCALES BASED ON EYE IRRITATION

Eye irritation is known to accompany photochemical smog although no clinical effects have been reported. The principal methods for measuring eye irritation were reviewed by Wayne, 1967 (47). These include intensity methods, threshold methods and response delay methods.

Intensity methods rate the severity of irritation after the subject has been exposed for a specific time. Threshold methods are based on determination of a minimum amount of irritant with which the panelist can detect irritation. The response delay method involves determination



of the time that lapses between exposure and onset of the irritation sensation.

In a study of hydrocarbon reactivity and eye irritation, Heuss et al, 1968 (19) found very poor correlation between chemical measurements such as NO oxidation or O₃ formation and eye irritation. They arrived at an eye irritation reactivity scale based on the average threshold response time. The scale is based on the equation:

$$\text{Eye Irritation Scale} = \frac{(240 - t) \times 10}{240}; \quad t = \text{average threshold response time (min.)}$$

Table 12-12 lists data reported by Heuss for a number of hydrocarbons according to eye irritation reactivity. The most reactive compounds (styrene, β -methylstyrene and alkylbenzene) are all capable of forming the very potent lachrymator, peroxybenzoyl nitrate. Benzene is fairly low in reactivity and the alkene, 2-methyl-2-butene, is also fairly low in contrast to its high relative reactivity in scales based on other criteria.

12.3.2.6 APPLICATION OF REACTIVITY SCALES

The utility of reactivity scales is in their application by regulatory agencies to control photochemical smog formation through selective restriction on the emissions of certain hydrocarbons to the atmosphere. The best known use of such emission control strategies is in the US through "Rule 66" (48). This regulation was designed for use in Los Angeles but it has been adopted (intact or slightly modified) by several agencies outside California. The primary emphasis of a "Rule 66" approach is to limit emissions of a few hydrocarbons (of high reactivity) much more severely



TABLE 12-12

EYE IRRITATION REACTIVITY

<u>HYDROCARBON</u>	<u>RELATIVE EYE IRRITATION REACTIVITY</u>
n-Butane	0
n-Hexane	0
Isooctane	0.9
tert-Butylbenzene	0.9
Benzene	1.0
Ethylene	1.0
1-Butene	1.3
Tetramethylethylene	1.4
cis-2-Butene	1.6
Isopropylbenzene	1.6
sec-Butylbenzene	1.8
2-Methyl-2-butene	1.9
trans-2-Butene	2.3
o-Xylene	2.3
p-Xylene	2.5
m-Xylene	2.9
1,3,5-Trimethylbenzene	3.1
1-Hexene	3.5
Propylene	3.9
Ethylbenzene	4.3
Toluene	5.3
n-Propylbenzene	5.4
Isobutylbenzene	5.7
n-Butylbenzene	6.4
1,3-Butadiene	6.9
α -Methylstyrene	7.4
Alkylbenzene	8.4
β -Methylstyrene	8.9
Styrene	8.9



than the emissions of other hydrocarbons (of low reactivity) Current restrictions on high reactivity compounds (nonexempt) is 15 lb/source/day and low reactivity compounds (exempt) is 3000 lb/source/day. Thus, this approach concentrates more on changing the character of emissions and is based on the premise that hydrocarbons of low reactivity do not significantly contribute to the formation of photochemical oxidants.

The so-called Appendix B approach developed by the US EPA and promulgated in 1971 (49) is part of the Requirements for Preparation, Adoption and Submittal of Implementation Plans. The emission limitations presented, represented, at the time, EPA's judgement of the degree of emission control which could be attained with a reasonable consideration of economic and technological aspects. With the exception of only a few "nonreactive" hydrocarbons, all emissions are considered as reactive.

Appendix B was not intended to require or encourage states to use this approach but rather to establish an information base on the extent to which emissions can be reduced from which implementation plans can be based.

Rule 66 is primarily directed towards reduction in photochemical smog formation near the source in urban areas by tightly controlling a few hydrocarbons of high reactivity. The possibility that low reactivity hydrocarbons may contribute to O_3 formation in areas distant from the emission source is not considered in Rule 66. Whether or not slow reacting hydrocarbons generate significant concentrations of O_3 is a complex question depending on a number of factors such as dispersion,



internal mixing, deposition mechanisms and other secondary compounds present. These factors and their effects are not well understood.

The "Appendix B" approach controls all but a few hydrocarbons known to be highly unreactive. No allowance is given for the differences between highly and moderately reactive hydrocarbons. This approach could be more effective than Rule 66 if low reactivity hydrocarbons are responsible for elevating O_3 concentrations in areas distant from the source.

The selection of a reactivity scale for use should relate to the effects which are to be controlled. With the exception of eye irritation scales, most other proposed scales are similar in their overall classification scheme, although there are differences in details.

Differences in scales result from the degree of validity of assumptions made (eg O_3 formation can be related only to OH attack rate, or can be based on complete degradation to CO_2 or formic acid, etc.) and the variation in smog chamber data. Such variation is a result of different physical characteristics for different chambers and differences in experimental conditions used. These problems in comparing and interpreting various smog chamber data are most difficult for low and moderately reactive hydrocarbons where longer irradiation times are required. However, this is the area where good data are most needed.

12.3.3 MEASURED AMBIENT AIR CONCENTRATIONS

There are relatively few reports in the literature of measurements of ambient concentrations of light aromatic hydrocarbons. This is partly



because in the past they were not believed to be as important as other classes of compounds and partly because of the difficulty in sampling and analysing for this mixture of similar compounds present at low concentrations.

Pilar et al, 1973 (50) studied the concentrations of benzene and toluene in Toronto at a number of locations and times during the day. They relate the observed levels of benzene and toluene to automobile emissions based on three factors: (1) the ratio of benzene to toluene, (2) the presence of distinct peak periods for both hydrocarbons at rush hour, and (3) the relative concentrations detected at various sampling stations. Aromatics have also been reported following studies in a number of cities: Los Angeles (51), Houston (52), Paris (53), Zurich (54), The Hague (55) and three South African cities (56). The results of these studies are summarized in Table 12-13. The figures presented are averages of hourly values. The measured levels varied widely depending on location and time. The maximum hourly average level of benzene and toluene observed in Toronto was 98 and 188 ppb respectively.

Pellizzari, 1977 (57) has reported studies of organic vapors at a number of sites in the U.S. characterized by a high concentration of chemical industrial activity. Only a fraction of the large number of organic compounds identified were quantitatively determined. The average concentration of benzene was 6 ppb with 50 ppb the maximum observed concentration. The average concentration of chlorobenzene and dichlorobenzene (when detected) was 0.2 and 0.5 ppb respectively. These levels for chloro- and dichlorobenzene varied widely and they were only detected



TABLE 12-13

AVERAGE MEASURED CONCENTRATIONS OF AROMATIC
COMPOUNDS IN AMBIENT AIR IN CITIES

(ppb)

<u>CITY</u>	<u>BENZENE</u>	<u>TOLUENE</u>	<u>ETHYLBENZENE</u>	<u>m- & p-XYLENE</u>	<u>o-XYLENE</u>
Toronto (50)	13	30			
Los Angeles (51)	15	37	6	22	8
Houston (52)	8	5	4	9	4
Paris (53)				1	0.5
Zurich (54)	54	39	8.7	30	9.3
The Hague (55)	8.9	17.9	3.1	12.4	3.1
Durban (56)	2.4	6.4	1.5	4.0	1.3
Pretoria (56)	5.8	8.7	3.2	4.0	1.8
Johannesburg (56)	3.4	10.3	1.9	4.5	1.6



in the vicinity of known industrial sources.

A comparison of benzene concentrations in major urban areas with high automotive densities and chemical industrial areas indicate at least as high or higher concentrations of benzene in urban areas as in industrial areas. Therefore population exposure to benzene vapors is expected to be strongly influenced by automotive densities.



12.4 AROMATIC COMPOUNDS IN WATER

12.4.1 AQUEOUS TRANSPORT, TRANSFORMATION AND REMOVAL

Organic compounds, once present in a water course, are subject to transport along the water body, dilution by turbulent mixing, chemical and physical transformation, biological degradation, and removal by adsorption on the bottom sediment or suspended particles and evaporation.

Many organic compounds such as benzene and toluene, etc. can readily be evaporated from one location, advected in an air mass to a new location and dissolved in another water body. Mackay et al, 1973 (58), using thermodynamic considerations, calculated evaporative half lives for a number of organic compounds in water bodies. Included in these calculations are the aromatics benzene, toluene, o-xylene, cumene, and naphthalene. Since the activity coefficients of these compounds in water are known, the equilibrium vapor composition of a water-hydrocarbon mixture above the water surface can be determined. The following assumptions are made:

- the organic compound is in true solution and not in suspension, colloidal, ionic, complexed or adsorbed form
- the vapor formed is in equilibrium with the liquid at the interface
- mixing in the water is sufficiently fast that the concentration at the surface is close to that of the bulk of the water
- the water evaporation rate is negligibly affected by the presence of the organic compound



Some of the results are presented in Table 12-14. Half lives range from about 14 min. for cumene to 2.9 hours for naphthalene. In situations where the water body is turbulent with frequent exchange between the surface water layer and the bulk, (for example in a fast-flowing shallow river or during white capping on a lake) the assumption of rapid mixing between the surface and the bulk of the water may be quite good. However, for other situations where such rapid mixing does not take place, the observed evaporation rate may be at least partially controlled by the liquid diffusion rate and as a result the observed evaporation rates may be lower than calculated.

In a later report, Mackay et al, 1975 (59) modified their earlier calculations on evaporative half lives to allow for partial liquid phase diffusion control. Use was made of mass transfer rates in water bodies as suggested by Liss et al, 1974 (60). This resulted in longer half lives as indicated in Table 12-14.

Adsorption of light aromatics on suspended particulate matter or in river sediments does not appear to take place to a significant extent (with the possible exception of naphthalene) since sediment samples analysed from waters known to carry these aromatic hydrocarbons have not shown detectable amounts to be present (61, 62).

The general environmental fate of the light aromatics considered here requires an assessment of the degradation processes of oxidation, hydrolysis and microbial action (apart from atmospheric reactions occurring in photo-chemical smog type reactions).



TABLE 12-14

CALCULATED EVAPORATIVE HALF LIVES OF AROMATICS
IN WATER BODIES AT 25 °C

<u>COMPOUND</u>	<u>$t_{1/2}$ (not liquid phase diffusion controlled)</u>	<u>$t_{1/2}$ (liquid phase diffusion partially controlling)</u>
Benzene	37.3 min.	4.81 hr.
Toluene	30.6 min.	5.18 hr.
o-Xylene	38.8 min.	5.61 hr.
Cumene	14.2 min.	5.79 hr.
Naphthalene	2.9 hr.	7.15 hr.



Biological oxidation of simple aromatic compounds has been studied and reported in a number of publications (63-71). Although many factors (such as moisture, pH, degree of aeration, presence of other nutrients and temperature, etc.) affect the biodegradability, the general observed rate of biodegradation of aromatics is slow. Even in activated sludges where microorganisms are acclimatized to aromatics, degradation is relatively slow.

Hydrolysis and oxidation reactions do occur but (with the possible exception of styrene) environmental conditions are not strong enough for these reactions to occur at significant rates.

12.4.2 MEASURED CONCENTRATION IN WATER

Organic compounds can enter raw water from a wide variety of sources which include:

- deposition from atmospheric sources
- leaching of naturally occurring organic matter
- contaminants introduced as the result of water treatment
- synthetic chemicals from industrial outfalls
- synthetic chemicals from other sources such as domestic sewage, storm sewer drainage, etc.

Up until only a few years ago, the main concern over effluent water quality has dealt with toxicity to fish or aesthetic considerations such as appearance, taste and odor. Before recent developments in analytical procedures for the determination of organics in water, taste and odor tests were the most sensitive methods available. Effluent guidelines



were often written in terms of fish toxicity tests or oxygen demand measurements such as COD and BOD.

These measurements are not satisfactory, however, since they do not relate well to the composition of the organic loading in the water sample, the source of contaminants, nor the potentially adverse effects on human health.

With the tremendous technical advances in analytical techniques such as gas chromatography and computer assisted mass spectrometry a large amount of data has been collected over the past few years on the levels of organics in water.

Most of these data are from surveys of water courses, industrial effluents or drinking water supplies and in many cases hundreds of compounds have been identified at trace levels. Aromatic compounds such as benzene, toluene, xylene, ethylbenzene and cumene, etc. are often reported in industrial effluents and also occasionally in drinking water supplies. Haloforms are frequently found in drinking water supplies. Most of the data available is qualitative in nature; however, some quantitative data are also available.

Novak et al, 1973 (72) report finding at least fifteen organic compounds in finished drinking water at levels between 0.1 and 60 $\mu\text{g/l}$. As a result of a US EPA study of drinking water in New Orleans, a preliminary report was released in 1974 (73) listing 66 organic compounds identified. These included several known or suspected carcinogens. Rook, 1972 (74) reported finding a number of organohalide and aromatic



compounds in treated water from the Rhine River. Grob, 1973 (75) and Grob et al, 1976 (76) report over 130 organic compounds present in Zurich tap water at an average concentration of 20 ng/l. These include organohalides and aromatic compounds.

Rook, 1974 (77) concluded from a study of water treatment processes that haloforms are formed during water treatment and are not present in raw water. This conclusion is supported by the reported observations of Bellar et al, 1974 (78) and later by others. These studies helped ensure the enactment of the U.S. Safe Drinking Water Act in 1974. One of the results of this Act was the expansion of the New Orleans study to the so-called "80 city survey" or the "National Organics Reconnaissance Survey" in which over 250 organic compounds were identified in drinking water around the U.S.A. (79). The US EPA is currently conducting a "National Organic Monitoring Survey", the object of which is to obtain data in support of the possible establishment of maximum contaminant levels of various organics in drinking water (80). A number of selected haloforms, aromatics, total organic carbon and other parameters are being determined. Of 113 cities surveyed, the analysis of drinking water showed benzene to be present at an average level of 0.2 $\mu\text{g/l}$ at seven sites.

In late 1974 and 1975, the Ontario Ministry of the Environment initiated a survey of organics in drinking water in Ontario and an investigation into organics in industrial effluents and sediment along the St. Clair River in the highly industrialized Sarnia area. Preliminary results have been reported (81, 61).

Along the St. Clair River, grab samples were taken of a number of plant effluents, and sediment samples were also taken at several sites (see



Table 12-15 and 12-16). Those effluent sample sites showing a significant organic content were resampled for quantitative analyses.

Of the 23 plant effluents reported, only 2 had high levels (ppm) of various aromatics. Four other sites showed ppb levels of some aromatics and the remaining 17 sites had no detectable amounts of benzene, toluene, xylenes, ethylbenzene, or styrene. None of these compounds were identified in sediment samples.

Since these were grab samples, they probably do not represent the average organic composition of the effluents sampled as most of the industrial sites do not operate in a steady state and rapid fluctuations in discharges can be expected. It is of interest, however, that most of the light aromatic hydrocarbons were not found to be accumulated on the river bed sediment.

Of the 48 water treatment plants sampled in the Ontario survey, 14 locations were selected for a GC/MS analysis. Five locations showed trace quantities (ppt) of aromatic hydrocarbons. These are listed in Table 12-17.

The water treatment plants at Brantford and Cayuga were further studied and the levels at Cayuga were found to be about 5 times higher than Brantford. In both cases no aromatics were found to be present in the raw water, yet the finished water contained aromatics.

Benzene and several alkylbenzenes in Cayuga's finished water were quantitated at the ng/l (ppt) level (see Table 12-18). No in-plant source of aromatic hydrocarbons were found. Although traces of aromatics



TABLE 12-15

QUANTITATIVE ANALYSIS OF AROMATIC HYDROCARBONS
IN PLANT EFFLUENTS

<u>EFFLUENT</u>	<u>AROMATIC HYDROCARBONS mg/l</u>				
	<u>BENZENE</u>	<u>TOLUENE</u>	<u>XYLENES</u>	<u>ETHYLBENZENE</u>	<u>STYRENE</u>
C-1	-	-	*ppb	-	-
C-2	-	-	-	-	-
C-3	-	-	-	-	-
C-4	-	-	-	-	-
C-5	-	-	-	-	-
C-6	30	25	25	6	200
C-7	-	-	-	-	-
C-8	-	-	*ppb	-	-
C-9	-	-	-	-	-
C-10	-	-	-	-	-
C-11	-	-	*ppb	-	-
F-2	-	-	-	-	-
I-2	-	-	-	-	-
I-8	-	-	-	-	-
K-1	-	-	-	-	-
K-2	-	-	-	-	-
K-3	-	-	-	-	-
K-4	149	12	5	-	-
K-5	-	-	-	-	-
K-6	-	-	-	-	-
K-7	*ppb	-	-	-	-
M-1	-	-	-	-	-
M-2	-	-	-	-	-

*ppb = not quantitated, concentration estimated at the 10-100 ppb levels.



TABLE 12-16

ORGANIC COMPOUNDS IDENTIFIED IN ST. CLAIRRIVER SEDIMENTS(by Gas Purging and Gas Chromatography-
Mass Spectrometry)

<u>LOCATION</u>	<u>COMPOUNDS IDENTIFIED</u>
SA-1	Dichlorobenzene
SA-2	Tetrachlorobutadiene Dimethylnaphthalene
SB-1	Tetrachloroethylene Hexachloroethane Pentachlorobutadiene Hexachlorobutadiene Dichlorobenzene Trichlorobenzene
SB-3	Tetrachloroethylene Hexachlorobutadiene Diethylbenzene Bromochlorobenzene
SB-4	Chloroform Carbon Tetrachloride Trichloroethylene Tetrachloroethylene Hexachloroethane Hexachlorobutadiene
SE	Alkanes
SH	None
SI	None
SJ	Alkanes



TABLE 12-17

TRACE ORGANICS APART FROM HALOFORMS IDENTIFIED
IN DRINKING WATER SUPPLIES

<u>LOCATION</u>	<u>FOUND</u>
Brantford	Benzene, Toluene, Ethylbenzene, Xylenes, Ethyltoluene, Diethylbenzene, Hexane
Cayuga	Benzene, Toluene, Xylenes, Ethylbenzene, Cumene, Ethyltoluenes, Diethylbenzenes
Goderich	Dichlorobenzene
Ottawa	Benzene, Toluene
Port Lambton	Methylene chloride, Tetrachloroethane, Xylenes
Smith Falls	Benzene, Toluene, Hexane
Union	Toluene, Ethylbenzene, Cumene



TABLE 12-18

AROMATIC HYDROCARBONS IDENTIFIED AT
CAYUGA WATER TREATMENT PLANT

<u>COMPOUND</u>	<u>RAW WATER</u>	<u>FINISHED WATER (ng/l)</u>
Benzene	nd	402
Toluene	nd	280
Ethylbenzene and/or <u>p</u> and <u>m</u> -xylene	nd	137
<u>o</u> -xylene	nd	46
Ethyltoluenes	nd	60
Diethylbenzenes	nd	16

nd = none detected at 15 ng/l detection limit.



were found in fresh filter media used in the treatment process (anthracite), this was not sufficient to account for the observed levels in the finished water.

It was speculated that if an occasional relatively high level of aromatics entered the treatment plant in the raw water then it would be adsorbed by the anthracite filter medium and subsequently desorb into the finished stream slowly over a period of time. Aliquots of used filter medium for the Cayuga treatment plant contained aromatics at levels nearly two orders of magnitude higher than fresh filter medium. Laboratory studies have been reported indicating that when water containing ppm levels of aromatics is introduced into a column of anthracite, aliquots of subsequent washes show a persistence of aromatics in the eluate at the ppt level (82).

In a recent publication, Sievers et al, 1977 (83) report that after chlorine gas is bubbled through samples of wastewater from Denver, toluene, ethylbenzene, and o-, m- and p-xylene are present in the treated water.

These compounds are present in much greater concentrations than in blanks or aliquots of the same samples prior to chlorination. The mechanism of formation and precursors are not known. More studies are required here.

In a recent study of five benzene producing or consuming plants in the U.S., Battelle, 1977 (84) found benzene levels in water ranging from less than one to 179 ppb in one plant's effluent. The concentrations at 13 upstream and downstream sample locations in nearby receiving waters, however, ranged from less than one to 13 ppb with an average of 4 ppb.



Jungclaus et al, 1978 (62) report a case study of the wastewater, receiving water and river sediments near a specialty chemicals manufacturing plant. Over 120 organic compounds were found in concentrations ranging up to 15 ppm. Results for benzene, toluene, xylenes and naphthalene are given in Table 12-19. With the exception of one measurement of naphthalene these compounds do not appear to accumulate in the river sediments.

An important, and often overlooked, factor concerning trace organics in water is that, in nearly all cases, only those compounds that are volatile enough to pass through a gas chromatograph are identified and measured. Because of these restrictions, normally less than 10-20 % of the total mass of organics in most waters are analyzed (85, 86). The light aromatics of interest in this report are all sufficiently volatile to be analysed.



TABLE 12-19

AROMATICS IN WATER AND SEDIMENT NEAR A
SPECIALTY CHEMICAL PLANT (ppm)

<u>COMPOUND</u>	<u>EFFLUENT</u>	<u>RIVER WATER</u>	<u>SEDIMENT</u>
Benzene	NQ	NQ	ND
Toluene	13-20	NQ	ND
Xylenes	NQ	NQ	ND
Naphthalene	104	0.006-0.01	1.5*

NQ = Present but not quantitated

ND = Not detected

* = detected in one sample only



12.5

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13 HEALTH EFFECTS



SECTION

PAGE NO.

13.1	INTRODUCTION	13-7
13.2	BENZENE	13-10
13.2.1	Summary of Biological Information	13-10
13.2.2	Metabolism	13-10
13.2.2.1	Absorption	13-12
13.2.2.2	Distribution and Retention	13-12
13.2.2.3	Elimination	13-14
13.2.3	Animal Experimental Studies	13-14
13.2.3.1	Hematopoietic System	13-14
13.2.3.2	Nervous System	13-20
13.2.3.3	Renal System	13-21
13.2.3.4	Gastrointestinal Tract	13-22
13.2.3.5	Liver	13-22
13.2.3.6	Cardiovascular System	13-25
13.2.3.7	Respiratory System	13-25
13.2.3.8	Reproductive System	13-25
13.2.3.9	Endocrine System	13-26
13.2.3.10	Eyes and Other Sense Organs	13-26
13.2.3.11	Carcinogenicity	13-26
13.2.3.12	Mutagenicity	13-27
13.2.3.13	Teratogenicity	13-28
13.2.3.14	Factors Affecting Toxicity	13-28
13.2.3.14.1	Tolerance	13-28
13.2.3.14.2	Susceptibility	13-29
13.2.3.14.3	Age	13-29
13.2.3.14.4	Sex	13-29
13.2.3.14.5	Seasonal Variations	13-29
13.2.3.14.6	Nutrition	13-30
13.2.3.14.7	Health of Individuals	13-30
13.2.3.14.8	Interaction with Other Chemicals	13-30
13.2.4	Human Experience	13-30
13.2.4.1	Epidemiological and Clinical Studies	13-31
13.2.4.2	Hematopoietic System	13-31
13.2.4.3	Nervous System	13-34
13.2.4.4	Renal System	13-35
13.2.4.5	Gastrointestinal Tract	13-35
13.2.4.6	Liver	13-36
13.2.4.7	Cardiovascular System	13-37
13.2.4.8	Respiratory System	13-37
13.2.4.9	Reproductive System	13-37
13.2.4.10	Endocrine System	13-38
13.2.4.11	Eyes and Other Sense Organs	13-38
13.2.4.12	Carcinogenicity	13-38
13.2.4.13	Mutagenicity	13-42
13.2.4.14	Teratogenicity	13-42
13.2.4.15	Factors Affecting Human Response	13-43



SECTION

PAGE NO.

13.2.4.15.1	Tolerance	13-43
13.2.4.15.2	Susceptibility	13-43
13.2.4.15.3	Age	13-44
13.2.4.15.4	Sex	13-44
13.2.4.15.5	Seasonal Effects	13-44
13.2.4.15.6	Nutrition	13-44
13.2.4.15.7	Health of Individual	13-44
13.2.4.15.8	Interaction with Other Chemicals	13-45
13.2.5	Evaluation of Health Risk to Man	13-45
13.3	TOLUENE	13-47
13.3.1	Summary of Biological Information	13-47
13.3.2	Introduction	13-48
13.3.3	Metabolism	13-48
13.3.3.1	Absorption	13-48
13.3.3.2	Distribution and Retention	13-49
13.3.3.3	Elimination	13-50
13.3.4	Animal Experimental Studies	13-51
13.3.4.1	Hematopoietic System	13-51
13.3.4.2	Nervous System	13-53
13.3.4.3	Renal System	13-55
13.3.4.4	Gastrointestinal Tract	13-55
13.3.4.5	Liver	13-55
13.3.4.6	Cardiovascular System	13-55
13.3.4.7	Respiratory System	13-56
13.3.4.8	Reproductive System	13-56
13.3.4.9	Endocrine System	13-56
13.3.4.10	Eyes and Other Sense Organs	13-56
13.3.4.11	Carcinogenicity	13-56
13.3.4.12	Mutagenicity	13-57
13.3.4.13	Teratogenicity	13-57
13.3.4.14	Factors Affecting Toxicity	13-57
13.3.4.14.1	Tolerance	13-57
13.3.4.14.2	Susceptibility	13-58
13.3.4.14.3	Age	13-58
13.3.4.14.4	Sex	13-59
13.3.4.14.5	Seasonal Variations	13-59
13.3.4.14.6	Nutrition	13-59
13.3.4.14.7	Health of Individuals	13-59
13.3.4.14.8	Interaction with Other Chemicals	13-59
13.3.5	Human Experience	13-60
13.3.5.1	Epidemiological and Clinical Studies	13-61
13.3.5.2	Hematopoietic System	13-62
13.3.5.3	Nervous System	13-64
13.3.5.4	Renal Effects	13-67
13.3.5.5	Gastrointestinal Tract	13-68
13.3.5.6	Liver	13-68



SECTION

PAGE NO.

13.3.5.7	Cardiovascular	13-68
13.3.5.8	Respiratory System	13-68
13.3.5.9	Reproductive System	13-69
13.3.5.10	Endocrine System	13-69
13.3.5.11	Carcinogenicity	13-69
13.3.5.12	Mutagenicity	13-69
13.3.5.13	Teratogenicity	13-69
13.3.5.14	Factors Affecting Human Response	13-69
13.3.5.14.1	Tolerance	13-70
13.3.5.14.2	Susceptibility	13-71
13.3.5.14.3	Age	13-71
13.3.5.14.4	Sex	13-71
13.3.5.14.5	Seasonal Effects	13-71
13.3.5.14.6	Nutrition	13-72
13.3.5.14.7	Health of Individuals	13-72
13.3.5.14.8	Interaction with Other Chemicals	13-72
13.4	XYLENE	13-73
13.4.1	Summary of Biological Information	13-73
13.4.2	Metabolism	13-73
13.4.2.1	Absorption	13-75
13.4.2.2	Distribution and Retention	13-75
13.4.2.3	Elimination	13-75
13.4.3	Animal Experimental Studies	13-76
13.4.3.1	Hematopoietic System	13-76
13.4.3.2	Nervous System	13-77
13.4.3.3	Renal System	13-79
13.4.3.4	Gastrointestinal Tract	13-79
13.4.3.5	Liver	13-80
13.4.3.6	Cardiovascular System	13-80
13.4.3.7	Respiratory System	13-80
13.4.3.8	Reproductive System	13-80
13.4.3.9	Endocrine System	13-81
13.4.3.10	Eyes and Other Sense Organs	13-81
13.4.3.11	Carcinogenicity	13-81
13.4.3.12	Mutagenicity	13-82
13.4.3.13	Teratogenicity	13-82
13.4.3.14	Factors Affecting Toxicity	13-82
13.4.3.14.1	Tolerance	13-82
13.4.3.14.2	Susceptibility	13-83
13.4.3.14.3	Age	13-83
13.4.3.14.4	Sex	13-83
13.4.3.14.5	Seasonal Variations	13-83
13.4.3.14.6	Nutrition	13-83
13.4.3.14.7	Health of the Individual	13-83
13.4.3.14.8	Interactions with Other Chemicals	13-83
13.4.4	Human Experience	13-84



SECTION

PAGE NO.

13.4.4.1	Epidemiological Studies	13-85
13.4.4.2	Hematopoietic System	13-85
13.4.4.3	Nervous System	13-86
13.4.4.4	Renal System	13-86
13.4.4.5	Gastrointestinal Tract	13-87
13.4.4.6	Liver	13-87
13.4.4.7	Cardiovascular System	13-87
13.4.4.8	Respiratory System	13-88
13.4.4.9	Reproductive System	13-88
13.4.4.10	Endocrine System	13-88
13.4.4.11	Eyes and Other Sense Organs	13-88
13.4.4.12	Carcinogenicity	13-89
13.4.4.13	Mutagenicity	13-89
13.4.4.14	Teratogenicity	13-89
13.4.4.15	Factors Affecting Human Response	13-89
13.5	NAPHTHALENE	13-90
13.5.1	Summary of Biological Information	13-90
13.5.2	Metabolism	13-90
13.6	CUMENE	13-94
13.6.1	Summary of Biological Information	13-94
13.6.2	Metabolism	13-94
13.7	STYRENE	13-97
13.7.1	Summary of Biological Information	13-97
13.7.2	Metabolism	13-97
13.7.2.1	Absorption	13-100
13.7.2.2	Distribution and Retention	13-101
13.7.2.3	Elimination	13-101
13.7.3	Animal Experimental Studies	13-101
13.7.3.1	Hematopoietic System	13-101
13.7.3.2	Nervous System	13-102
13.7.3.3	Renal System	13-102
13.7.3.4	Gastrointestinal Tract	13-102
13.7.3.5	Liver	13-103
13.7.3.6	Cardiovascular System	13-103
13.7.3.7	Respiratory System	13-103
13.7.3.8	Reproductive System	13-103
13.7.3.9	Endocrine System	13-103
13.7.3.10	Eyes and Other Sense Organs	13-103
13.7.3.11	Carcinogenicity	13-104
13.7.3.12	Mutagenicity	13-104
13.7.3.13	Teratogenicity	13-105
13.7.3.14	Factors Affecting Toxicity	13-105
13.7.3.14.1	Tolerance	13-105
13.7.3.14.2	Susceptibility	13-106
13.7.3.14.3	Age	13-106



SECTION

PAGE NO.

13.7.3.14.4	Sex	13-106
13.7.3.14.5	Seasonal Variations	13-106
13.7.3.14.6	Nutrition	13-106
13.7.3.14.7	Health of Individual	13-106
13.7.3.14.8	Interaction with Other Chemicals	13-106
13.7.4	Human Experience	13-107
13.7.4.1	Epidemiological and Clinical Studies	13-107
13.7.4.2	Hematopoietic System	13-109
13.7.4.3	Nervous System	13-109
13.7.4.4	Renal System	13-110
13.7.4.5	Gastrointestinal Tract	13-110
13.7.4.6	Liver	13-110
13.7.4.7	Cardiovascular System	13-111
13.7.4.8	Respiratory System	13-111
13.7.4.9	Reproductive System	13-111
13.7.4.10	Endocrine System	13-111
13.7.4.11	Eyes and Other Sense Organs	13-111
13.7.4.12	Carcinogenicity	13-112
13.7.4.13	Mutagenicity	13-112
13.7.4.14	Teratogenicity	13-112
13.7.4.15	Factors Affecting Human Response	13-112
13.7.4.15.1	Tolerance	13-112
13.7.4.15.2	Susceptibility	13-112
13.7.4.15.3	Age	13-112
13.7.4.15.4	Sex	13-113
13.7.4.15.5	Seasonal Effects	13-113
13.7.4.15.6	Nutrition	13-113
13.7.4.15.7	Health of the Individual	13-113
13.7.4.15.8	Interaction with Other Chemicals	13-113
13.8	ETHYLBENZENE	13-114
13.8.1	Summary of Biological Information	13-114
13.8.2	Introduction	13-114
13.8.3	Metabolism	13-114
13.8.4	Acute Toxicity	13-115
13.8.5	Skin Penetration	13-115
13.8.6	Human Experience	13-115
13.9	REFERENCES	13-116



13.1 INTRODUCTION

The data in this section are drawn from a variety of sources such as animal studies, short term human experiments, accidents, and experience derived from occupational exposures. Very seldom is there information derived from situations which duplicate life time community exposures. Therefore, almost all judgements about the actual or potential health effects of the compounds in this report when considered as air pollutants involve varying degrees of extrapolation and these in turn must be based on certain assumptions.

An effort has been made to highlight those health concerns which can reasonably be related to the anticipated level of exposure of the general population to the particular pollutant. If the possible health effect is serious, attention has been drawn to it even if the projected level of exposure of the community is well below the level at which the effect has been found. Particularly for agents that have been shown to cause cancer, or are suspected carcinogens, a straight line relationship between dose and effect has been assumed.

There is no entirely satisfactory method of handling the question of the highly variable response to be expected among any group of humans subjected to the same level of pollutant. This matter is usually handled by using a "safety factor" in setting standards but it is generally recognized that this is an arbitrary procedure with little scientific data upon which to base the calculations. It has



not been within the terms of reference of these reports to suggest air quality standards but rather to set out the health data available at this time that can be used as one input into the standard setting process.

Comment on the Summary of Biological Information

Appended to a Consideration of Each Pollutant

To be useful a summary must be short, but the abbreviations carry with them considerable risks, since by dropping information on experimental conditions, the variability of the effects measured, and a host of other qualifying factors, an appearance of precision and authority is given to the data which is seldom warranted. It is hoped that the rating system will only be used in setting priorities and that it will be constantly reviewed to allow consideration of new data.

Obviously, such a cryptic rating system as that used in this summary of the biological effects of the selected chemicals contains a considerable measure of subjective judgement. By using only three rating categories (A, B, and C), it is hoped that enough information is provided for a simple ranking of chemicals to be undertaken on the basis of their biological actions. This ranking can then be compared with other ordering systems based on such characteristics as production, emission levels, etc.

A further advantage of a very simple system of assigning categories lies in its obvious limitations, which, because they are obvious, may serve as a warning that the data upon which the categories



are based is very seldom complete and/or are often not of a uniformly high quality. It is particularly important to bear this caveat in mind with regard to data derived from human experience, where the investigator must work with the available information which has usually been collected for quite other reasons than those motivating his own study.

Note also that the biological rating system refers only to toxicity which is the ability to cause harm after reaching the target organ of organism. The more important factor upon which to base policy and administrative decisions is related to the hazard to health that a chemical poses. Hazard is an expression of the probability that a chemical will reach the target organ or organism in sufficient quantity to cause harm. Hazard must take into account such factors as the spatial and temporal relationships between the emissions and the receptor, transport factors, numbers of receptors, etc.

Of the three letters used for ranking, A represents the highest toxicity and C the lowest.



13.2 BENZENE13.2.1 SUMMARY OF BIOLOGICAL INFORMATION

At low levels irritating to nose and eyes, narcotic at higher levels; can cause aplastic anemia and there is some epidemiological evidence that it may cause leukemia in man. Data inadequate to establish dose-response relationships at concentrations of benzene found in ambient air.

Toxicity Rating: [A]

Low acute toxicity but given [A] rating because chronic exposure may lead to aplastic anemia and/or leukemia.

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low (produces narcosis)
Chronic	High (depression of bone marrow)

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	Not relevant in view of epidemiological evidence
Epidemiological	(high) [A] (carcinogen)

13.2.2 METABOLISM

A large percentage of the benzene that is absorbed into the body is excreted unchanged, through the lungs, in the exhaled air. The percentage excreted in this manner has been reported to vary from 15 to 60 percent (1). That benzene which is not excreted through the lungs is converted, probably via an epoxide step, to phenol. The



initial reaction is mediated by a mixed-function oxidase which is inducible by pre-treatment with benzene, phenobarbital or 3-methylcholanthrene (2). Although phenol has been found to be the primary metabolite of benzene, some metabolism of the epoxy compound takes place with the formation of phenyl mercapturic acid or the formation of catechol by dehydrogenation of benzene glycol formed from the hydration of the benzene epoxide.

The phenol formed may be conjugated with sulfuric acid (sulfo-conjugation) or with glucuronic acid (glucuro-conjugation). The phenylsulfuric and phenylglucuronic acids are excreted in the urine in the form of alkaline salts. In experiments in which fifteen human volunteers were exposed to benzene at a concentration of a hundred parts per million for five hours a day, 46 percent of the benzene was retained, and of that amount 61 percent was recovered as phenol, 6.3 percent as catechol, and 2.5 percent as hydroquinone, Teisinger et al, 1952 (3).

The excretion of phenol in the urine following benzene exposure has often been used as a measure of the severity of the exposure. Maximum concentrations occur within two hours after exposure, Hunter, 1968 (4).

Benzene may also be detected in the expired air 24 hours after exposure has ceased, and it has been suggested that serial measurements of benzene in the expired air could be used to estimate the level of benzene exposure by extrapolation backwards to the cessation of the exposure. For further discussion of the metabolism of benzene see Section 13.2.3.5.



13.2.2.1 ABSORPTION

Benzene is readily absorbed through the lungs. A single exposure of five to ten minutes in an atmosphere of 66 mg per litre (20,625 ppm) has proved fatal, Gerarde, 1963 (5). Death is due to the anaesthetic effect of benzene, with incoordination, stupor, coma, convulsions, paralysis and death.

Benzene when swallowed by mouth causes local irritation to the mucous membranes of the mouth, throat, esophagus and stomach. The absorption of the swallowed benzene leads to signs and symptoms of systemic benzene intoxication. The swallowing of as little as a tablespoonful of benzene has been followed by collapse, bronchitis and pneumonia, (6), Averill, 1889 (7).

Skin contact with benzene may cause reddening and blistering of the skin and a dry, scaly dermatitis may follow prolonged or repeated exposure. Experiments in which the arms or whole body surface of male human subjects were exposed to cotton soaked in benzene for twenty to thirty minute periods were not followed by any observable change in the urinary excretion ratio of inorganic sulfate to total sulfate, a change in the ratio being used as evidence of the absorption of benzene, Cesaro, 1946 (8). Other similar experiments exposing the skin to benzene and attempting to measure benzene in the expired air have also failed to show any appreciable absorption of benzene through the skin (9).

13.2.2.2 DISTRIBUTION AND RETENTION

In a study reported in 1950, 23 human volunteers were exposed to



benzene concentrations ranging from 47 to 110 ppm. The volunteers breathed the benzene and air mixture for periods varying from two to three hours, during which time samples of inhaled and exhaled air were taken every fifteen minutes and analysed. Blood and urine samples were also taken and analysed. The absorption of benzene was shown to be greatest during the first five minutes and rapidly decreased thereafter, becoming constant approximately fifteen minutes after the onset of exposure. At the end of one hour, approximately 50 percent of the inhaled benzene was absorbed. After the exposure was completed, 30 to 50 percent of the absorbed benzene was eliminated through the lungs, 0.1 to 0.2 percent was eliminated unchanged through the kidneys and the remainder was metabolized (9).

Retention* of benzene has also been measured in 6 Japanese students (3 males and 3 females) exposed to 52-62 ppm benzene for 4 hours. Percent retention of benzene decreased with exposure time and reached a constant level during the fourth hour of exposure. The percent retention of toluene became constant during the third hour and was higher at 36.6 % than that for benzene (30.2 %). The value for benzene is lower than the 46-80 % reported by other investigators, Nomiya et al, 1974 (10). The difference in reported time to constant percentage absorption between the Japanese study and that of Srbova reported in the NIOSH criteria document (9) may be explained by differences in technique, eg length of breath holding in the two studies.

* Retention = % retention R which equals $\frac{C_i - C_e}{C_i} \times 100$

Where C_i = concentration of solvent in inspired air

C_e = concentration of solvent in expired air



Benzene saturation of the circulating blood is reported to be very rapid, reaching 70 to 80 percent saturation within thirty minutes after the beginning of the exposure. Complete saturation may require as much as two to three days, however, due to the fact that fatty tissue, which has a great affinity for benzene, has a rather poor blood supply and requires a relatively long period to attain equilibrium between the level of benzene in the blood and the level of benzene in the fat, Gerarde 1963 (5).

13.2.2.3 ELIMINATION

The major route of elimination for benzene is through the lungs. In the study of Japanese students previously referred to, the rate of decay of benzene in the expired air after the end of exposure was measured and the data fitted to a mathematical equation. The rate constants for 0-1, 1-5 and 4-17 hours after cessation of exposure were calculated and were found to be 3.66, 0.737 and 0.0158 respectively for men and 3.02, 1.09 and 0.0429 respectively for women. These differences between the sexes were not significant (10). Small quantities of benzene are excreted by the kidney in the unaltered state and the rest excreted by the kidneys after oxidation to phenols and diphenols and excreted as such or conjugated with sulfate ions in the liver and then excreted as esters of glucuronic and sulfuric acid.

13.2.3 ANIMAL EXPERIMENTAL STUDIES

13.2.3.1 HEMATOPOIETIC SYSTEM

Although benzene, like toluene, may cause depression of the central



nervous system, with incoordination, stupor, progressing to coma and finally to death, it is the effect of benzene on the bone marrow which has brought about the greatest concern, and it is upon this effect that modern benzene standards have been based.

Exposure to benzene vapor produces a reduction in the number of white cells circulating in the blood which is related to the concentration of benzene to which the animals are exposed. In rats exposed to 831, 65, and 61 ppm of benzene, reduction in the white cell count began after seven hours a day, five days a week exposure. Exposure to mean concentrations of 47 and 44 ppm with the same exposure periods produced a moderate but definite lowering of the white cell count after five to eight weeks of exposure. No such drop was found in rats exposed to average concentrations of 31, 29 or 15 ppm benzene, Diechman et al, 1963 (11). Rats exposed to 1000 ppm benzene in air for 23.5 hours per day showed serious deterioration in condition after 183 hours of exposure. In addition to the reduction of the number of white cells in the blood, levels of DNA in the bone marrow were reduced and the number of red cell precursors was increased. When the rats were removed from the benzene exposure, the abnormalities in the blood returned to normal but the levels of DNA in the bone marrow remained depressed. In exposures to 200 ppm and 50 ppm, the white cell activity of the bone marrow was reduced but the red cell activity was increased (12). In studies in which bone marrow cells were grown in tissue culture from benzene-treated mice, the number of colonies of granulocytic cells formed was used as a measure of the number of granulocyte precursors in the bone marrow. This assay was called the colony-forming cell assay (CFC). The formation of stem cells in



cultures of bone marrow was also used and referred to as the colony-forming unit assay (CFU). The assay involved injecting bone marrow cells from benzene-treated animals into x-ray irradiated mice and evaluating the subsequent formation of colonies on the spleen of the receptor mouse. One day after the mice were exposed to 4,680 ppm of benzene for eight hours, both CFC and CFU activity was reduced to 40 to 45 percent of that measured in control animals, Uyeki et al, 1977 (13).

Mice and rats exposed to benzene at 100 and 300 ppm showed the expected overall depression of white cell levels, but the lymphocytes were generally depressed, while granulocytes were not. The mice, but not the rats, showed a reduction in red cell count which became apparent at the same time as the white cell depression (12).

While most recent experiments have involved the inhalation of benzene, the earliest experiments demonstrating depression of bone marrow activity were carried out in 1916 in rabbits which were given benzene dissolved in olive oil by subcutaneous injection at a dose of 1 ml per kg of body weight per day. The white cell counts were then monitored until they were reduced to a level of 200 to 800 cells per cu. mm. The sensitivity of the animals varied, with some reaching these levels in four and others taking as long as nine days (12).

Several investigators have studied the recovery of the white cell count after discontinuing exposure to benzene and their findings agree that the white cell count shows an initial rise and then a secondary



depression before returning gradually to control values. In severe acute exposure, or in lower levels of exposure maintained for long periods of time, complete aplasia of the bone marrow has been found.

As a part of such studies, one investigator determined the ability of the bone marrow to regenerate after benzene exposure and found that the animals showed regeneration only to the extent of forming primitive reticular cells. Although the most prominent effect of benzene exposure is depression of the white cell count, reductions in hemoglobin, red cells, reticulocytes and thrombocytes are also observed. After treatment of animals with radioactive thymidine, radioautography of the bone marrow showed that incorporation of radioactivity into DNA was reduced, Moeschlin et al, 1967 (14).

Studies of the incorporation of radioactive iron into circulating red cells demonstrated that benzene depresses such incorporation. Based on present knowledge of the formation of red cells in the mouse, such data suggest that the cells most sensitive to benzene are early precursors called pronormoblasts and normoblasts. Toluene protected against the benzene-induced depression of the uptake of radioactive iron by the red cells and reduced the levels of benzene metabolites in bone marrow without affecting the level of benzene present in the bone marrow. These studies suggest that toluene exerts its protective effects by inhibiting benzene metabolism, and that a metabolite of benzene may be the cause of the toxic action of benzene on the bone marrow. Earlier studies designed to investigate the mechanism of benzene toxicity have



usually focused on the liver as the probable source of toxic metabolites, and support for this approach has been provided by the protective effect of phenobarbital through the stimulation of hepatic microsomal enzymes. Studies concentrating on the metabolism of benzene in the bone marrow may be more relevant in explaining the bone marrow depression, Andrews et al, 1977 (15).

Benzene given by mouth is the least investigated of the various exposure routes. One investigator gave 132 feedings of benzene to rats at doses of 1, 10, 50 and 100 mg per kg of body weight over a period of 187 days. No effects were observed at the 1 mg per kg level. Slight depression of the white count was found after the 10 mg per kg dose, and both anemia and depression of the white count were found after the higher doses.

Although the hematological findings in animals would appear to support the hematological findings in humans, some inconsistencies remain to be explained. For instance, the finding that while the total white cell counts were depressed in rats and mice, the number of granulocytes was reported to remain constant. Since depression of the granulocytes would reflect bone marrow damage, this suggests a discrepancy with human experience in which depression of granulocytes is a consistent and important finding.

Although aplastic anemia is a serious consequence of chronic benzene exposure in humans, it is the production of leukemia that has been of greatest concern in considering the human health risks of benzene.



Leukemia has not been produced in animals by skin painting, inhalation or oral dosing (12).

Although chemicals can cause leukemia in both mice and rats, only one report has been found claiming leukemia in mice after treatment with subcutaneous injections of benzene for 17 to 21 weeks(12). Of the 44 mice that survived treatment, eight were described as having developed leukemia or lymphosarcoma. However, this investigator did not include control mice in the study and failed to provide details concerning the strain of mice and the criteria for establishing the diagnosis of leukemia. (An attempt to duplicate the results of this experiment under carefully controlled conditions, using a number of different strains of mice, failed to demonstrate either aplastic anemia or leukemia after weekly injections of benzene 30 mg per kg of body weight throughout the animals lifetime (12)).

The relatively low frequency of leukemia in benzene-exposed human populations may help to explain the failure of animal studies to duplicate the human experience since very large numbers of animals would be needed to provide a sufficient number of treated and control animals. The other reasons that an animal model has not yet been found for the leukemia established to occur in man from benzene exposure may be due to: a unique metabolic pathway in man, less efficient repair of the benzene-caused damage to DNA in man, or the ability of the human system to detect neoplastic cells may be relatively more susceptible to damage by benzene in man than in other animals.



13.2.3.2 NERVOUS SYSTEM

Benzene is a nervous system depressant regardless of whether the compound is inhaled, swallowed or injected. The average time for rabbits inhaling 35 to 45 thousand parts per million of benzene vapor to become lightly anaesthetized was 3.7 minutes. In five minutes they exhibited excitability and tremors, and death occurred in approximately 36 minutes at this concentration, Carpenter 1944 (16). In Russian experiments, a delay in conditioned response time was reported in rats exposed to 20 ppm of benzene six hours a day, six days a week for five and a half months, but rats exposed to 4 ppm of benzene for the same time period did not show such a delay in the conditioned response (17). In experiments in Japan, mice exposed six hours a day for 20 days to benzene concentrations of 100 ppm showed a decrease on the fifth day in spontaneous wheel-turning activity, Horiuchi et al, 1967 (18). Similar alterations in conditioned reflexes have been observed by other Russian authors (17).

In a comparison of the central nervous effects of a group of selected hydrocarbons, it was found that exposure to 10,000 ppm of benzene caused dyspnea, twitching of the whiskers and ataxia, followed by hyperreactivity to auditory stimuli. There were rigid tail and carpopedal spasms with generalized quivering at 30 minutes. Violent twitching appeared at intervals after 40 minutes, and this picture remained unchanged for about two hours except for an increase in the violence of the twitches, which occurred once or twice per minute. The rats at this concentration of benzene salivated profusely and the skin felt cooler than normal to



the touch. Rats exposed to 20,000 or 40,000 parts per million of benzene showed the same picture, but it developed more rapidly and there were some deaths before the two hours had elapsed. In a similar experiment conducted with toluene, there was more evidence of irritation at the 10,000 ppm level, and although there was central nervous system depression there was no quivering or twitching, and no hyper response to auditory stimuli.

Electroencephalographic studies with benzene showed that at a concentration of 10,000 ppm there was no change in the EEG over a period of about one hour in rats, and when the concentration was increased to 25,000 ppm, high voltage slowing appeared in the record. The frequency was about 3 per second with potentials of about 200 microvolts, as compared to the resting frequency of 5 per second with a 75 microvolt potential. About half an hour after the cessation of exposure, the record approached normal with slightly lower potentials and a frequency of about 4 per second. A concentration of 30,000 ppm of benzene caused convulsive twitching in ten minutes. In this series of experiments, which also included studies with para-xylene, para-ethyltoluene, para-methylstyrene, para-cymene, para-tertiary-butyltoluene and meta-tertiary-butyltoluene, benzene was the least toxic as far as its effect on the central nervous system was concerned, followed by toluene. Central nervous system toxicity increased with molecular weight, but not in direct order, Furnas et al, 1958 (19).

13.2.3.3 RENAL SYSTEM

Both acute and subacute exposure to benzene has resulted in histochemical changes in the kidneys of rats and mice, Snyder et al, 1975 (20).



Renal effects were found at high levels of exposure and are not considered important compared with the central nervous system depression and the effect on the hematopoietic system.

13.2.3.4 GASTROINTESTINAL TRACT

The oral route is the least investigated in studies of benzene toxicity, and no local effects on the gastrointestinal tract have been reported. About 1 percent of the administered dose of benzene has been found to be excreted in the bile, Abou-El-Marakem et al, 1967 (21).

13.2.3.5 LIVER

Benzene hydroxylation occurs in liver microsomes of rabbits, rats and mice, and requires oxygen and NADPH. Benzene reacts with cytochrome P450 to yield a Type I spectral change indicative of the formation of an enzyme substrate complex, and with cytochrome P448 to yield a Type R1 spectral change in much the same manner as that found with many other substrates for the mixed-function oxidases. Aniline and aminopyrine, both of which inhibit the metabolism of other compounds by cytochrome P450 or interact with cytochrome P450, also inhibit benzene metabolism, Gonasun et al, 1973 (22). Benzene hydroxylase, like other microsomal hydroxylases, is inducible. Benzene oxide, which is thought to be the important intermediate in the metabolism of benzene has not been demonstrated in liver microsomes, probably because of its extreme lability, but naphthalene oxide was recovered when naphthalene, an aromatic hydrocarbon closely related to benzene, was incubated with liver



microsomes, Gillette et al, 1957 (23). The addition of benzene oxide, however, to a liver microsomal preparation results in the products of benzene metabolism, Jerina et al, 1968 (24).

The hepatic microsomal mixed-function oxidase system can be stimulated by enzyme induction by at least two general classes of compounds, polycyclic aromatic hydrocarbons and phenobarbital, plus a number of other compounds which act in a similar manner. Benzene hydroxylase activity in vitro increases after treating animals with phenobarbital or 3-methylcholanthrene, a polycyclic aromatic hydrocarbon. Administration of benzene itself or dimethylsulfoxide also increases the rate of benzene metabolism, Snyder et al, 1967 (25). Induction by benzene is characterized by an increase in metabolism and in the incorporation of amino acids into microsomal protein within 24 hours of a single dose, but there is no proliferation of smooth endoplasmic reticulum at that time. After one or two weeks of benzene treatment, however, the smooth endoplasmic reticulum appears to be proliferated and the metabolism of benzene continues to be slightly stimulated. These observations suggest that there does not seem to be a relationship between the degree of proliferation of smooth endoplasmic reticulum and the rate of benzene metabolism.

It has been reported that young rats display a high rate of benzene metabolism in vitro and were more susceptible to benzene given subcutaneously than old rats, in which the rate of benzene metabolism was slower. It was also demonstrated that 3-amino-1,2,4-triazole, which inhibits benzene metabolism in rat liver homogenates, protected against benzene toxicity.



It was therefore concluded that a metabolic product of benzene was responsible for benzene toxicity, Nomiyama, 1965 (26).

Further studies showed that rats treated with phenobarbital metabolized more benzene and were more resistant to benzene-induced leukopenia. These results suggested that metabolism of benzene was a detoxifying process and the inhibition of benzene metabolism should result in increased toxicity. There appears to be a common theme in all of the studies mentioned above, since in each case the effects of benzene on a parameter of bone marrow activity were correlated with the rate of benzene metabolism, either in vivo or in vitro using liver preparations. Although there is considerable suspicion that benzene metabolism plays a role in benzene toxicity, there is good reason why the evidence is not yet definitive. The study of benzene metabolism, whether in vivo or in vitro, has actually been a study of events that occur in the liver. The liver is responsible for most of the metabolism of benzene, and the metabolites of benzene in the urine are essentially the results of hydroxylation and conjugation in the liver. However, benzene toxicity is manifested in the bone marrow rather than in the liver. It must either be argued that a toxic metabolite travels from the liver to the bone marrow or that the metabolite is indeed formed in the bone marrow. If benzene oxide is the active metabolite, its chemical reactivity is too great for it to survive transport through the circulation.

It appears, then, that although the liver may serve as a good model for study of the enzyme systems which metabolize benzene, the most profitable tissue for studying the role of benzene metabolism in toxicity is the bone marrow itself.



13.2.3.6 CARDIOVASCULAR SYSTEM

There have been a few reports of sudden death following acute inhalation of benzene in man, but no investigations of this effect in animals has been found. It has been assumed that such deaths have been due to cardiac arrhythmias similar to those that occur under conditions of unusual exertion or excitement with a variety of halogenated hydrocarbon solvents.

13.2.3.7 RESPIRATORY SYSTEM

No reports of adverse effects of benzene on the respiratory system have been found.

13.2.3.8 REPRODUCTIVE SYSTEM

No reproductive study of animals exposed to benzene has been found but in a study designed to investigate the possibility that pregnant animals were more susceptible to the toxic effects of benzene than non-pregnant animals, guinea pigs were given subcutaneous daily injections of 0.1 gm/kg of benzene in olive oil for nine weeks during pregnancy and red cell and white cell counts were made before, during, and after pregnancy. The study concluded that pregnancy did not enhance the toxic effects of benzene upon the hematopoietic system, Desoille et al, 1967 (27).

Rabbits exposed to 80 parts per million benzene for 243 days showed slight degeneration of the seminiferous tubules of the testes and similar changes were found in guinea pigs exposed to 88 parts per million of benzene for 269 days, Wolf et al, 1956 (28).



13.2.3.9 ENDOCRINE SYSTEM

No reports of adverse effects of benzene on the endocrine system have been found.

13.2.3.10 EYES AND OTHER SENSE ORGANS

50 percent of rats exposed to 50 parts per million benzene for 600 hours were reported to show bilateral cataracts. However, cataracts were not found in rats exposed to 200 parts per million of benzene in the same 8 hour a day, five day a week protocol even after 750 hours of exposure, Nau et al, 1966 (29).

The occurrence of cataracts at the low concentration and not at the high concentration and the lack of confirmation of this report by other investigators suggests that the possibility that benzene causes cataract formation in rats should be treated with caution at this time.

Benzene is reported to have an odor threshold of 4.68 parts per million, which is very similar to that of toluene, but is much higher than substituted benzene derivatives which may have odor thresholds as much as a thousand fold lower depending on the nature of the substituent group, Leonardos et al, 1969 (30).

13.2.3.11 CARCINOGENICITY

Apart from the one uncorroborated finding of leukemia in rats after prolonged benzene exposure, no other evidence of a carcinogenic effect of benzene in animals has been found.



13.2.3.12 MUTAGENICITY

That benzene is a mitotic poison has been demonstrated in a number of experiments. These studies have included whole animal exposures as well as the effect of benzene on cells in vitro.

Rats exposed to 300 or 100 parts per million of benzene showed a persistent increase in chromosome breaks and aneuploidy (deviation from the normal diploid chromosome number) in the bone marrow of treated (300 parts per million) animals. The increase following 100 parts per million exposure was not as great and not of clear statistical significance (12). Increased chromosome breakage in several species has also been reported. Rats exposed to benzene subcutaneously over a period of 12 days showed highly significant increases in chromosome aberrations of bone marrow cells over untreated and toluene treated controls, Lyapkalow 1973 (31). In reviewing the studies carried out in animals it is clear that different exposure times in different species can induce increases in chromosome aberrations, but there is no clear evidence of a dose dependent response to benzene exposure. It also seems probable that the effects observed are more likely to be due to direct toxic damage than to mutational damage. Very few of the studies have involved inhalation exposure, and the relevance of direct injection of benzene to the problems of occupational exposure may be questioned.

Studies of dividing erythroblasts taken from the amphibian newt have demonstrated anaphase abnormalities. Young animals were injected with water saturated with benzene and were then bled six to twelve hours later, a culture being taken from a drop of tail blood at that time. Examination



of the blood showed 28 % anaphase abnormalities, 38 % of mitoses arrested in late metaphase, while observations over several hours showed that these mitotic abnormalities resulted in unequal nuclear divisions, polynucleated cells, and atypical nuclei. Prophase and early metaphase anomalies were never found at the doses used in these studies (up to 54 mg of benzene per animal) (12).

13.2.3.13 TERATOGENICITY

No reports on teratogenicity were found.

13.2.3.14 FACTORS AFFECTING TOXICITY

13.2.3.14.1 TOLERANCE

As mentioned earlier, pre-treatment of animals with phenobarbital increases the rate of hepatic microsomal metabolism of benzene as much as tenfold, but on the basis of the LC_{50} and the LD_{50} the animals were not affected by the increased rate of benzene metabolism.

It has also been found that benzene itself rather than its hydroxylated derivatives is capable of causing liver microsomal stimulation, Saito et al, 1973 (32).

Toluene, however, protected against the benzene induced depression of red cell iron uptake and reduced the level of benzene metabolized in the bone marrow without affecting the level of benzene in the tissues. It would appear from this study that toluene exerts protective effect on benzene toxicity by inhibiting benzene metabolism, Andrews et al, 1977 (15).



13.2.3.14.2 SUSCEPTIBILITY

An interaction between benzene and radiation has been suggested by retrospective studies of the survivors of the two atomic bombings in Japan, however, no studies of combined exposure to radiation and to benzene have been found in animals.

Pregnancy has not been found to enhance the toxic effect of benzene in guinea pigs although inadequate dietary protein intake was found to increase the susceptibility of dogs and rats to benzene poisoning (17).

It has been reported that young rats display a high rate of benzene metabolism in vitro and are more susceptible to benzene given subcutaneously than old rats in which the rate of benzene metabolism was slower, Snyder et al, 1975 (20). In rats exposed to benzene at 1,000 parts per million for seven hours a day, five days a week, the order of increasing sensitivity to benzene based on depression of white cell counts was adult males, young males, adult females, young females, Ikeda 1964 (33).

13.2.3.14.3 AGE

See Section 13.2.3.14.2

13.2.3.14.4 SEX

See Section 13.2.3.14.2

13.2.3.14.5 SEASONAL VARIATIONS

No information on seasonal variations of benzene toxicity were found.



13.2.3.14.6 NUTRITION

See Section 13.2.3.14.2. Experimental studies with dogs and rats have shown that in inadequate protein intake predisposes them to increased susceptibility to benzene poisoning. However, there appeared to be no appreciable effect of varying the fat content of the diet, Shils et al, 1949 (34)

13.2.3.14.7 HEALTH OF INDIVIDUALS

As might be expected the decreased circulating white cells in benzene poisoning have been found to lower the resistance of animals to infections (10).

13.2.3.14.8 INTERACTION WITH OTHER CHEMICALS

Apart from the reactions with phenobarbital and toluene previously referred to, few other studies of the interaction of benzene with other chemicals in animals has been found. In a study of the joint toxic action of perchloroethylene with benzene, it was found that mixtures of perchloroethylene and benzene gave values for LD₅₀ in rats which was slightly less than the LD₅₀ for each compound given separately, Withey et al, 1975 (35)

13.2.4 HUMAN EXPERIENCE

Several experimental studies involving human exposure to benzene have been reported and these have been incorporated into the text under the appropriate heading, eg absorption by inhalation.



13.2.4.1 EPIDEMIOLOGICAL AND CLINICAL STUDIES

Although the acute effects of benzene poisoning, with its main effect being the narcotic action on the nervous system, are important and can result in fatalities under conditions of high exposure, it is the effect of long exposure to benzene on the hematopoietic system that causes the greatest concern. Therefore the results of epidemiological studies will be found in the following section and under 13.2.4.12 CARCINOGENICITY.

13.2.4.2 HEMATOPOIETIC SYSTEM

The ability of chronic exposure to benzene to depress the number of formed elements in the blood has been known since 1897 when four cases of fatal aplastic anemia were reported in workers making bicycle tires. Since that time, there have been many case reports and epidemiological surveys of workers exposed to benzene which have confirmed the association between the blood findings and the exposure to benzene. This confirmation has been most convincing in those cases where the appearance of the pancytopenia has been related to the beginning of benzene exposure and where the effect on the blood ceased with the replacement of benzene by other solvents. It is thought that the ability of benzene to affect erythrocytes, granulocytes and thrombocytes is due to their common origin from a pluripotential cell in the bone marrow. This cell is believed to be able to differentiate into the precursors of the various formed elements and that benzene is toxic to this cell. There is some evidence that this cell may in turn derive from another pluripotential cell which can differentiate into either lymphocytic or myelocytic precursors. This



may be of importance in considering benzene toxicity since a reduction in lymphocytes is frequently observed in pancytopenic persons with a history of benzene exposure. Chromosomal abnormalities have also been reported in circulating lymphocytes in persons with chronic benzene exposure and such chromosomal abnormalities have been associated with an increased risk of lymphocytic neoplasms.

The early symptoms of pancytopenia are principally due to the anemia with resulting tiredness, easy fatigability, malaise, dizziness, headaches, palpitations and shortness of breath. In more severe cases, bleeding is a prominent feature due to thrombocytopenia, and in severe cases death may occur due to hemorrhage or to overwhelming infection. In some persons there may be apparent recovery from the pancytopenia with the later development of fatal acute leukemia. The thrombocytes may show the greatest percentage reduction in which case the condition is referred to as thrombocytopenia, while virtual absence of all formed elements is referred to as aplastic anemia.

In many cases of benzene exposure, individual cytopenias have been reported, eg leukopenia without anemia or without thrombocytopenia.

Despite the voluminous literature, the relationships between the level of benzene, the effect produced and the duration of the exposure are still not well enough understood to provide a "no-effect" level.

There appears to be a range of effects which progress from small qualitative disturbances through reductions in the numbers of one or more of the formed elements of the blood and ending in aplastic anemia. As



will be discussed in a later section, aplastic anemia may in turn be followed by leukemia.

Investigators are not yet in agreement as to the earliest changes in the blood that can be attributed to benzene. One of the more sensitive indicators appears to be the phagocytic function of the leukocytes. This function has been reported to be decreased in workers having a benzene exposure ranging between 24 and 39 parts per million over a five year period.

Other investigators have reported an increase in the level of red cell delta-aminolevulinic acid (a precursor in the synthesis of heme). This effect was reported to occur in workers having an earlier benzene exposure ranging between 6 and 15 parts per million and more recently having an average exposure of about 1.6 parts per million. A number of French investigators have reported decreased leukocyte alkaline phosphatase in workers exposed to benzene levels ranging from 10 to 25 parts per million. At slightly higher exposures there appears to be general agreement among most investigators that leukopenia and/or thrombocytopenia becomes increasingly common with the exposure level.

The prognosis in mild cases of pancytopenia is reported to be good following the discontinuance of benzene exposure. In some individuals, however, pancytopenia has progressed even after the cessation of exposure and in some cases apparent recovery from the pancytopenia has been followed by acute leukemia after an interval of 15 to 27 years (12).

One study re-evaluated a group of individuals exposed to benzene in



a shoe factory, where benzene had been in use for about ten years and average levels of 400 parts per million benzene had been measured. At the time of the original investigation 107 of the 147 workers studied showed abnormal blood counts, of which the most common was thrombocytopenia. In the follow-up study, 125 of the original workers were restudied nine years after the cessation of benzene exposure and it was found there was a definite improvement in the mean platelet count, however, the platelet count in the group which had been exposed to benzene remained significantly lower than that of a control group of workers who had never been exposed to benzene. One of the workers who had been most severely affected at the time of the original investigation showed gradual improvement of his blood picture which had returned to normal two years after the original study, but this was later followed by the onset of acute leukemia. These findings suggest the recovery after benzene toxicity may occur very slowly or may be incomplete, Hernberg et al, 1966 (36).

The relationship of benzene exposure to leukemia will be discussed under Section 13.2.4.12 CARCINOGENICITY.

13.2.4.3 NERVOUS SYSTEM

Benzene has a narcotic effect on man similar to that of anaesthetic agents such as chloroform.

Exposure to massive concentrations, in the region of 2.5 % volume in air has been rapidly fatal. Mild exposures produce exhilaration followed by giddiness, headache, nausea, incoordination and unconsciousness, Browning, 1965 (37).



Some investigators have reported that nervous irritability and unsteadiness in walking may persist for periods of two to three weeks following severe exposure to benzene and that single exposures to benzene vapor at 20,000 parts per million may be fatal within five to ten minutes; 7,500 parts per million will produce toxic effects if inhaled for half to one hour and an exposure to 3,000 parts per million may be tolerated for up to one hour, Gerarde, 1960 (38, 9).

13.2.4.4 RENAL SYSTEM

No information specifically incriminating benzene in the production of renal disease was found; one reference refers to glomerulonephritis in patients with a history of extensive long term exposure to solvents. This was a retrospective study and hydrocarbon solvents were not specifically identified but many petroleum products were included. The mean period of solvent exposure in one group of 28 patients with advanced proliferative glomerulonephritis was significantly greater than in a group of 35 patients with other forms of renal disease. Benzene was not specifically mentioned as one of the hydrocarbon solvents, Bierne et al, 1972 (39), Ehrenreich, (40).

13.2.4.5 GASTROINTESTINAL TRACT

Oral ingestion of benzene causes local irritation of the mouth, throat, esophagus and stomach, followed by absorption of the benzene from the stomach and the systemic symptoms of benzene poisoning. The swallowing of as little as a tablespoonful of benzene has been known to cause collapse, bronchitis, and pneumonia (6, 7).



13.2.4.6 LIVER

From animal studies it has been determined that benzene metabolism occurs to a very large extent in the liver and that this metabolism depends on the dose given and the presence of compounds which either stimulate or inhibit benzene metabolism. For obvious reasons much less is known of the details of benzene metabolism in humans compared with animals such as the rat and the mouse. What information is available is consistent with that obtained from animals. One major difference appears to be in the percentage of benzene excreted from the lungs, one investigator finding that this is no more than 12 percent of the retained dose of benzene, a value significantly less than that found in animals which are normally found to excrete 50 to 70 percent of the retained dose through the lungs, Hunter et al, 1972 (41).

Measurements of phenol in the urine of human volunteers indicated that 50 to 87 percent of the retained benzene was excreted as phenol. The highest concentrations of phenol were found in the urine within about three hours from the termination of the exposure. In one extensive study the metabolism of phenol was studied in 19 species including man.

¹⁴Carbon-phenol was given orally to a man at a dose of 0.01 mg/kg of body weight. The major route of metabolism in all species was conjugation and in man this route was principally through the production of the ethereal sulfate, Capel et al, 1972 (42).

As pointed out above under the section on animal studies, because the main impact of benzene is upon the hematopoietic system, studies of the metabolism of benzene in the liver may not be as relevant as similar



studies carried out in the bone marrow. This is particularly important because of the possibility that a short-lived metabolite of benzene is responsible for the hematopoietic effect and that this metabolite may be benzene oxide, the reactivity of which would preclude its transport from the liver to the bone marrow.

13.2.4.7 CARDIOVASCULAR SYSTEM

There are a number of scattered reports in the literature which suggest that sudden exposure to high concentrations of benzene particularly in situations associated with excitement or with exertion may result in sudden death. Such deaths are thought to be due to sensitization of the myocardium to circulating catecholamines with resultant fatal arrhythmias (37, 43, 44).

13.2.4.8 RESPIRATORY SYSTEM

Apart from the well known hazard of aspiration pneumonitis common to many surface active hydrocarbons, no reports of other effects of benzene on the lung were found.

13.2.4.9 REPRODUCTIVE SYSTEM

In the older literature, it was commonly stated that women were more susceptible to benzene poisoning than men, but in the more recent literature this suggestion has not found much support although one report in 1956 states that women are more susceptible to benzene poisoning particularly when they are pregnant. However, the study involved women exclusively, and no firm conclusions may be drawn from this report regarding sex differences in susceptibility to benzene poisoning (9).



13.2.4.10 ENDOCRINE SYSTEM

No reports on the effect of benzene on the endocrine system in man were found.

13.2.4.11 EYES AND OTHER SENSE ORGANS

Since skin contact with liquid benzene may cause redness and blistering of the skin, it is to be expected that contact with the eyes would cause intense irritation and unless immediately treated might lead to permanent damage, but no references to damage to the eyes were found in the literature.

13.2.4.12 CARCINOGENICITY

There is now considerable epidemiological evidence that benzene can cause leukemia in humans. However, no animal model has yet been developed for benzene as a carcinogen and this places benzene in an unusual category perhaps only shared with arsenic among agents known to cause neoplasms in man but not so far in animals.

The information linking benzene to leukemia is of two main types. The first are case reports of which there are now well over 100 since the original report in 1928.

The second source of evidence results from epidemiological studies and here three general approaches have been used. The first has been a comparison of the number of cases of leukemia occurring in persons having a history of occupational exposure to benzene compared with the incidence of leukemia in the general population, or some other occupational group not exposed to benzene. The second approach has been to study the occupational



histories of persons with leukemia and compare the incidence of benzene exposure in these persons with the incidence in a control population. The third and last approach has been to study the causes of death in populations working in industries involving benzene exposure and in particular to study the incidence of leukemia in such groups.

One important series of studies were those carried out in Turkey among shoe workers exposed to benzene, Aksoy et al, 1974 (45). 150 cases of leukemia attributed to benzene were identified in Italy, Vigliani et al, 1976 (46).

A study of workers in the U.S. rubber industry showed a 54 % increase in the death rate for cancers of the lymphatic and hematopoietic system in male rubber industry workers dying in 1950 as compared with workers in all other manufacturing industries (47).

A study of the mortality experience of a large number of male workers in four tire manufacturing plants showed that mortality due to all causes was normal or only slightly elevated, whereas deaths due to cancer of the lymphatic and hematopoietic system were 31 % higher than expected. Similarly deaths due to all forms of leukemia were also elevated and when this category was further subdivided the overall standardized mortality rate for lymphatic leukemia was found to be 158. It is particularly interesting that the standardized mortality rate for lymphatic leukemia was 291 in the age group 40 to 64. As might be expected in a study of this type in which the causes of death among rubber workers were being studied, the increased incidence of deaths due to leukemia could not with certainty be attributed to benzene since the workers were



exposed to other solvents as well.

A particularly important study is that conducted among workers making Pliofilm in which benzene was used as a solvent. The investigators studied the causes of death among 748 white male workers engaged in the pliofilm operation. The control groups were selected from the general population of U.S. white males and a group of 1,447 white males employed in the same State and over the same time period but with no known exposure to benzene. Among the 140 deaths reported, 9 were due to lymphatic and hematopoietic cancer compared with 3.45 based on expectations for U.S. white males and 5.10 expected in the control working population not exposed to benzene. Of the 9 deaths due to lymphatic and hematopoietic cancer, 7 were due to leukemia as opposed to 1.38 and 1.48 expected on the basis of the respective control groups. While the size of this group is not particularly large, what makes the study of considerable value is that it provides the most information about the relationship between the disease and the exposure to benzene. However, this study underlines the general inadequacy of the benzene exposure data for all the studies because, in the investigation just mentioned, the frequency of air sampling was less than once per month and there is evidence in the reports that concentrations were being reduced over the period of the study. The report states that in most instances the benzene levels ranged from 0 to 10 or 15 parts per million. Despite these deficiencies, which are present in almost all such studies, the Pliofilm workers exposed to benzene had an estimated ten-fold greater risk of dying from myelogenous and monocytic leukemia than persons not so exposed, Infante et al, 1977 (48). In commenting on the Pliofilm study,



it has been noted that the workers may in fact have been exposed to concentrations of benzene well below the acceptable industrial hygiene limits, which range from 100 parts per million maximum allowable concentration in 1941 to 10 parts per million as a time weighted average in 1971. It is also possible that these individuals were exposed to concentrations well above the permissible concentrations, which were not detected in the relatively infrequent monitoring surveys. For instance, workers having to enter the spreader and drying units to remove damaged film and to repair mechanical failures might spend 30 minutes in the units and sampling inside these units indicated levels of benzene ranging from 200 to 350 parts per million (12). The results of the Pliofilm study were used as the basis for an extrapolation of the leukemia risk to the low levels of general population exposure, which averages one part per billion benzene, Mara et al, 1977 (49). A linear non-threshold model was used for the extrapolation. Such a model may be expected to give an upper limit to the estimated risk. Using this extrapolation model, the carcinogen assessment group of the U.S. Environmental Protection Agency estimated that the number of cases of acute myelogenous and monocytic leukemia per year in the general population due to ambient atmospheric benzene would be somewhere between 30 and 80 cases. The lifetime risk to an individual continually exposed to benzene at a level of 1 part per billion is estimated to be between 10^{-5} and 2.5×10^{-5} depending on which exposure assumptions are made in the Pliofilm study. The carcinogen assessment group consider that these figures are not likely to be exceeded and that the risk could be lower.



The writers of the Benzene Health Effects Assessment Document for the U.S. Environmental Protection Agency, conclude that "the available literature concerning the benzene level associated with the development of acute leukemia is inadequate for generation of dose-response curves or for analysis of risk related to dose" (12).

13.2.4.13 MUTAGENICITY

The available documentation strongly suggests that chromosome breakage and damage may persist in hematopoietic and lymphoid cells after exposure to benzene. A dose-dependent relationship between exposure to benzene and amount of chromosome damage has not been demonstrated. Evidence that benzene causes disturbance in DNA synthesis suggests that its mutagenic action could involve interference with mitosis. Many authors have suggested that the lack of an observed dose-response relationship in benzene induced chromosome damage is due to variation in individual susceptibility. Some studies have recorded biological effects at chronic exposure levels below 25 parts per million of benzene. The variable response to benzene may be attributed also to such possibilities as activation of virus, suppression of immune surveillance, or co-carcinogenic activity of other chemicals. Because benzene has not so far been found to cause leukemia in animals, the relationship between benzene exposure, chromosome changes and leukemia remains undetermined.

13.2.4.14 TERATOGENICITY

No evidence of teratogenicity in humans has been found in the literature; however, there are a few scattered case reports of pregnancy



occurring in women suffering varying degrees of benzene poisoning. In one case a women was found to be eight months pregnant when admitted to hospital for treatment of pancytopenia after occupational exposure to benzene. Although severely pancytopenic, the patient delivered an apparently normal boy. The following year the patient had another pregnancy and delivered a normal baby girl. A cytogenic study performed on the peripheral blood of the newborn boy did not indicate any chromosomal abnormalities, Forni et al, 1971 (50).

13.2.4.15 FACTORS AFFECTING HUMAN RESPONSE

13.2.4.15.1 TOLERANCE

There is great variation in the response of human populations to exposure to benzene, but the reasons for this variation are not known although many investigators have postulated some persons having a particular susceptibility to benzene intoxication.

13.2.4.15.2 SUSCEPTIBILITY

An interaction between benzene and radiation in the causation of leukemia is suggested by a retrospective study of the survivors of the two atomic bombings in Japan. Comparisons of the control and leukemic patients revealed that the risk of leukemia was 2.5 times higher in those with an occupational history potentially related to benzene or x-rays. The risk was significantly higher in those with five or more years of potential exposure, but not in those who had been employed in such occupations for less than five years.



13.2.4.15.3 AGE

Most investigators are in general agreement that susceptibility to benzene poisoning is not related to age, Smith, 1928 (51), Savilahti, 1956 (52).

13.2.4.15.4 SEX

Although in the early literature women are considered to be more susceptible to benzene poisoning than men, none of the recent studies confirm this finding and in those with references under age above, sex differences in susceptibility were not found.

13.2.4.15.5 SEASONAL EFFECTS

Only one report suggesting increased toxicity of benzene at elevated environmental temperature on benzene toxicity has been found, Koslova, 1969 (53).

13.2.4.15.6 NUTRITION

No reports of the effect of nutrition on benzene toxicity in humans were found.

13.2.4.15.7 HEALTH OF INDIVIDUAL

There is conflicting evidence as to whether persons with beta-thalassemia minor, an inherited disorder of hemoglobin synthesis, may have an increased risk from benzene poisoning, Aksoy et al, 1975 (54). If this greater susceptibility is confirmed, this might indicate that the more rapidly proliferating bone marrow, which is part of the thalassemia syndrome, increases the risk of hematopoietic cell damage due to benzene.



13.2.4.15.8 INTERACTION WITH OTHER CHEMICALS

While it is possible that the diet or the ingestion or inhalation of drugs or chemicals might modify the metabolism of benzene and its toxicity, at present the information is too meagre for the identification of such individual factors.

13.2.5 EVALUATION OF HEALTH RISK TO MAN

Benzene, although similar in its depressant effect upon the central nervous system to the closely related solvents toluene and xylene, differs from them in its ability to cause reduction in the formed elements of the blood after long exposure. In some cases this reduction can proceed to aplastic anemia which, if not treated, results in death from anemia, overwhelming infection or bleeding. In some cases there is substantial epidemiological evidence that benzene can cause leukemia in man although this has not so far been demonstrated in animals.

Although the reason that the chronic toxicity of benzene differs from that of xylene and toluene is not certain, it appears probable that it is related to its metabolism. Benzene is thought to yield a short lived but highly reactive metabolite, benzene oxide, and it is this compound which is thought to be responsible for the enhanced toxicity of benzene compared with toluene and xylene.

In attempting to relate the levels of benzene in the air to the risk of leukemia, the common problem of lack of adequate exposure information makes any such effort virtually impossible at this time. In no study so far reported can it be stated that exposure to benzene was never significantly above 50 ppm and yet resulted in leukemia.



The converse is also true that it is impossible to prove that all of the cases of leukemia that developed after exposure to benzene were exposed at some time to levels well in excess of 50 ppm, although this seems probable from the nature of the operations in the plant. In the face of this uncertainty about the relationship between the level of benzene and the neoplastic response in man, it is only prudent to attempt to eliminate all unnecessary exposure to benzene and where some exposure is unavoidable to keep the exposure to the lowest practicable level.



13.3 TOLUENE13.3.1 SUMMARY OF BIOLOGICAL INFORMATION

Irritant to nose and eyes at about 200 ppm. Onset of "drunkenness" (central nervous system depression) at about 400 ppm. Irreversible effects not reported in range of average present occupational exposures (up to 100 ppm); toluene in early studies often contaminated with benzene. Odor threshold 4-5 ppm.

Toxicity Rating: [C]

No evidence of chronic effects at levels up to 100 ppm TWA in occupational exposure. There are no reports at present suggesting that lifetime exposure at the levels of toluene currently encountered in the ambient environment would exert a harmful effect on health. As with any such statement, it may require modification in the light of new knowledge. In particular the possibility of synergistic effects of toluene with other agents having an effect on the central nervous system should be recognized and information on such effects should be sought.

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	Low

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	Low
Epidemiological	Low



13.3.2 INTRODUCTION

While it is always important to know the purity of materials used experimentally and to identify as precisely as possible any contaminants they contain, until recently the biological actions of toluene and benzene were considered so similar that investigators seldom thought it necessary to state the purity of the toluene used. With the great concern over the effects of benzene on the hematopoietic system and the possibility that this effect is not shared to the same extent by toluene, the degree of purity of toluene used in experiments becomes much more important and the lack of this information in much of the earlier work is frustrating but understandable.

13.3.3 METABOLISM

13.3.3.1 ABSORPTION

Absorption from the Lungs

Toluene vapor is rapidly absorbed by inhalation, but little quantitative data exists describing the relationships between concentration, time and absorption. By analogy with other similar compounds, such as benzene, rapid uptake into the blood would be expected. This rapid uptake phase would be almost complete in five to ten minutes and would cease after approximately half an hour of exposure at which time the level of toluene in the blood and air would approach equilibrium. The succeeding slow phase of absorption may last 2-3 days if a constant level of exposure is maintained. This period of slow absorption is due to the relatively poor blood supply to much of the fatty tissue in the body which, despite the great affinity of toluene for fat, results in the blood supply



being a limiting factor in reaching an equilibrium state between the level of toluene in the blood and that in the fat (58).

Absorption Through the Skin

Toluene is not well absorbed through the intact skin in either the liquid or the vapor phase, Gerarde (55, 56).

Absorption from the Gut

Daily doses of 10 grams of toluene in olive oil have been reported to have been given to humans for 3 weeks without "adverse symptoms" (57).

An "absolute lethal" dose of 8 grams of toluene per kg body weight was found in rats when the compound was given by mouth.

No other information on the effect of short term oral administration, either experimental or accidental, was found. (For long term feeding studies see Section 13.3.4.11)

13.3.3.2 DISTRIBUTION AND RETENTION

Toluene, being of low solubility in water and very soluble in fat, accumulates in subcutaneous fat, brain, bone marrow, adrenal gland and deposits of adipose tissue throughout the body. As was mentioned under Section 13.3.3.1, because of the relatively poor solubility in blood, toluene equilibrates rapidly between the air and blood, but due to the relatively poor perfusion of many fatty tissues, equilibration between the levels in the blood and fat may take several days under conditions of constant and uniform exposure. If toluene were not metabolized, a similar long period would be required to reach equilibrium after exposure has ceased, but according to metabolic studies this is not the case. About



70 % to 80 % of the absorbed toluene is excreted as hippuric acid. This leaves about 20 % to 30 % which is excreted unchanged through the lungs. For the reasons already stated, this 20 % to 30 % of the toluene absorbed may be released from the body fat stores and excreted in the breath over several days. Such a situation might be expected to result in continuing central nervous system effects for this length of time if the earlier exposure had been to a high level of toluene and this is confirmed in the following study. In controlled exposures of three humans for 8 hours, twice weekly, for three months, 200 ppm of toluene resulted in after-effects including: fatigue, general confusion, moderate insomnia, and restless sleep. At 800 ppm the exposure could only be maintained for 3 hours due to nervous system toxicity and the after-effects, including moderate to severe insomnia, lasted several days, Von Oettingen et al, 1942 (58, 59).

13.3.3.3 ELIMINATION

About 20-30 % of the toluene absorbed is excreted unchanged through the lungs. The remaining 70-80 % is metabolized to benzoic acid by oxidation of the methyl group. Conjugation of the benzoic acid with glycine to form hippuric acid results in a compound with sufficient water solubility for it to be excreted in the urine. Since hippuric acid is a normal constituent of urine and is a metabolite of food containing benzoates or benzoic acid, the levels found in urine fluctuate widely due to these dietary components and the measurement of hippuric acid in the urine is an unreliable index of exposure to toluene.



Induction of liver enzymes by phenobarbital and other inducers of liver enzymes accelerates the metabolism of toluene and therefore increases its elimination in the urine thus shortening the duration of any effects of toluene on the central nervous system. There is some evidence that in rats, at high doses of toluene, an additional metabolic pathway may come into play resulting in the increased urinary excretion of organic sulphate, Gerarde, 1960 (55). When both toluene and benzene are given to rats at the same time, the toluene appears to interfere with the metabolism of benzene as demonstrated by a decrease in the expected amount of phenol excreted, phenol being a major metabolite of benzene but not of toluene (56).

13.3.4 ANIMAL EXPERIMENTAL STUDIES

13.3.4.1 HEMATOPOIETIC SYSTEM

Because toluene, unless prepared with special care, may contain significant amounts of benzene, and because benzene has pronounced deleterious effects on the hematopoietic system, only those experiments in which toluene of a high degree of purity has been used should be considered in reaching conclusions about the toxicity of toluene to the hematopoietic system.

Toluene purified by distillation caused no deaths in guinea pigs submitted to 18, daily, four hour exposures up to 1250 ppm. Exposure to 1000 ppm for 4 hours per day for 35 days also was without effect on the hematopoietic system (60).

Exposure of 2 dogs to 99.9 % pure toluene (containing less than



0.1 % benzene) 8 hours per day, six days per week for four months to 2000 ppm and then to 2660 ppm for two additional months, showed no effect on the hematopoietic system (56). Rats exposed to 200, 1000 and 2000 ppm of 99.9 % pure toluene (containing less than 0.2 ppm benzene) 8 hours per day for 32 weeks also showed no effect on the hematopoietic system (56).

One study, of particular interest in making a judgement on the toxicity of toluene to the hematopoietic system, investigated the effect of pure toluene on the synthesis of deoxyribonucleic acid (DNA) in the cells of the bone marrow and the circulating cells of the blood. The rate of synthesis was measured by the uptake of tritium labelled thymidine. The toluene was injected subcutaneously into rabbits at a rate of 300 mg per kilogram of body weight per day for six weeks or 700 mg per kilogram of body weight for up to nine weeks. No depression of bone marrow function, as measured by the uptake of radioactive thymidine, was found. In a duplicate of this experiment, rats given the same doses of benzene developed aplastic anemia, and autoradiography of the bone marrow showed marked inhibition of DNA synthesis. These results strongly support the concept that toluene is not toxic to the bone marrow and in this, it differs from benzene, Spec et al, 1968 (61).

No other studies using toluene of high purity and of sufficient duration for an effect to be detected, if present, were found and so on the basis of the data available it appears that toluene of high purity does not affect the cellular components of the blood or the bone marrow under the experimental conditions described.



13.3.4.2 NERVOUS SYSTEM

Toluene has a narcotic pharmacological action on the central nervous system. Using toluene "concentrate" containing 0.06 % by volume benzene, but 51 % paraffins and naphthenes, rats remained normal throughout a four hour exposure to 1700 ppm (6-8 mg/litre). At 3300 ppm (13 mg/litre) the rats showed slight loss of co-ordination while at 6300 ppm (25 mg/litre) tremor of the head was seen at 1 hour and prostration occurred in 2 hours. Three hours after exposure at this concentration, the rats had returned to a normal state.

In the same study, 2 beagle dogs exposed to 1500 ppm (6 mg/litre) showed slight watering of the eyes and tremor of the head. The tremor of the head persisted when the concentration was reduced to 1000 ppm (4.1 mg/litre) but two other beagles exposed to 760 ppm (3 mg/litre) showed no evidence of nervous system depression.

As a further extension of these same series of experiments, four cats who inhaled a concentration of 7800 ppm (31 mg/litre) became lightly anaesthetized after 2 hours of exposure. Slight loss of co-ordination was noted after 20 minutes of exposure at this concentration, Carpenter et al, 1976 (62).

It is of interest that in one set of experiments exposure of rats to 5000 ppm and after 20 minutes to 10,000 ppm of "chemically pure" toluene did not result in deaths and the level was then raised to 20,000 ppm. After 25-30 minutes at this concentration the rats were deeply anaesthetized and stopped breathing. Although the description of the experimental design of this experiment is confusing and the results incorrectly reported in the NIOSH Criteria Document on Toluene, the



findings do in general support the onset of depression of the central nervous system in rats at a concentration of about 3,000-4,000 ppm. At a level of 6,000-7,000 ppm both rats and cats show light anaesthesia. Profound anaesthesia appears in rats between 10,000 and 20,000 ppm. No histological changes were reported in the brains of the rats in the experiments conducted by Furnas and Hine (19) at any concentration of toluene tested.

In exposures of several days, Batchelor (63) found that exposure to toluene (purity not stated) at a level of 1600 ppm for 18-20 hours per day caused rats to show irritation of the mucous membranes, conjunctivitis, incoordination and light narcosis. By the third day the animals showed mild twitching, general increase in tone of the body musculature and a drop in body temperature of 7 °C. They then developed great weakness and died during the third day. At concentrations of 1250 ppm, slight instability and incoordination appeared but apart from some irritation of mucous membranes the animals appeared normal. Below 1100 ppm the animals showed no abnormal signs. Longer exposures of up to 13 weeks, 6 hours per day, five days per week, at concentrations of 980, 480 and 240 ppm did not result in any detectable harm to rats or beagle dogs, Carpenter, 1976 (62). The toluene in these experiments is referred to as "toluene concentrate", and while it contained only 0.06 % by volume of benzene, it contained 38.69 % paraffins and 15.36 % naphthenes, the inhalation exposure being therefore only 46 % toluene, ie less than half of the vapor to which the animals were exposed.



13.3.4.3 RENAL SYSTEM

No reports of damage to the kidneys of animals exposed to toluene were found.

13.3.4.4 GASTROINTESTINAL TRACT

No reports of injury to the gastrointestinal tract were found but it should be noted that no reports of animal studies were found in which the toluene was given by mouth.

13.3.4.5 LIVER

Apart from the metabolic studies reported in Section 13.3.3.3, no reports of liver damage in animals exposed to toluene were found.

13.3.4.6 CARDIOVASCULAR SYSTEM

No histological changes have been found in the hearts of animals exposed to toluene and the only changes in heart function due to toluene have been those reported by Taylor and Harris (64) in experiments designed to reproduce some of the conditions associated with the sudden deaths of humans sniffing the fumes from model airplane glue. Several of these glues contain toluene and in experiments on mice it was found that exposure to the fumes of glue or toluene caused sinus bradycardia, increase in the P.R. interval and atrio-ventricular block. These results support the thesis that certain sudden deaths after solvent inhalation in humans may be due to cardiac arrhythmias.



13.3.4.7 RESPIRATORY SYSTEM

Apart from some evidence of irritation of the nose of rats at concentrations of 1,600 ppm of toluene of unrecorded purity (56) no adverse affects of toluene on the respiratory system have been found.

13.3.4.8 REPRODUCTIVE SYSTEM

No studies were found in which the effect of toluene on reproduction in animals had been studied.

13.3.4.9 ENDOCRINE SYSTEM

No studies of the effect of toluene on the endocrine system were found.

13.3.4.10 EYES AND OTHER SENSE ORGANS

When 0.1 ml of undiluted toluene was introduced into the right eye of rabbits, a barely perceptible irritation of the conjunctival membrane was noted within 1 to 4 hours in 3 of the 6 animals tested. Observations were made at 24, 48 and 78 hours after treatment. Examination of the cornea with sodium fluorescein solution revealed no evidence of even superficial necrosis in any of the treated eyes (56).

13.3.4.11 CARCINOGENICITY

No studies have been located in which the potential carcinogenicity of toluene when applied to the skin was specifically studied, but in one investigation toluene was used as a vehicle for applying graded doses of benzo[a]pyrene. The mice used in this study received drop applications



of the solvent mixture on the shaved, interscapular skin 3 times per week until they died or a persistent skin tumour developed. Three strains of mice were used but the number of animals in each group was small (20, 17 and 17). However, not only were no tumours found in the toluene treated controls but tumours were not found in animals receiving 0.15 mg of benzo[a]pyrene (a known carcinogen) as well as the toluene.

Only one experiment was found in which toluene was given by mouth and the animals examined for tumours. 138 daily feedings of 118, 354 and 590 mg/kg body weight of toluene were given by gastric intubation and observations of the test animals for 193 days showed no evidence of tumours grossly or on microscopic examination, Wolf (28).

13.3.4.12 MUTAGENICITY

Damage to bone marrow chromosomes has been reported in one study of rats injected subcutaneously with toluene of unspecified purity at a rate of 1 mg/kg each day for 12 days. Similar experiments using 0.8 g/kg for 12 days induced metaphase aberrations and chromosomal breaks in the lamina cells of the bone marrow (57).

13.3.4.13 TERATOGENICITY

No evidence that toluene is a teratogen was found but it must also be noted that the appropriate tests do not appear to have been conducted.

13.3.4.14 FACTORS AFFECTING TOXICITY

13.3.4.14.1 TOLERANCE

Animals pre-treated with phenobarbital, which induces liver enzymes,



metabolize toluene more rapidly and therefore can tolerate somewhat higher doses and recover more quickly from the narcotic effect (see Section 13.3.3.3).

That toluene itself may induce liver enzymes is suggested by the observation that rats exposed to 13 ppm (49.6 mg/m^3) 5 hours per day, 6 days per week for 6 months showed increased metabolism of toluene. This effect was not seen at 40 ppm (153 mg/m^3), 5 hours per day, 2 days per week, due apparently to decreased protein synthesis and therefore impaired metabolism of toluene (57).

13.3.4.14.2 SUSCEPTIBILITY

While no animal data suggesting particular susceptibility was found, other than that concerned with age, factors interfering with the metabolism of toluene in the liver might be expected to render an animal more susceptible to the toxic effects of toluene.

13.3.4.14.3 AGE

In studies comparing the acute oral LD_{50} toxicity of toluene in rats at 14 days of age with the LD_{50} in young adult (80-160 g body wt.) and older rats (300-470 g body wt.), toluene was significantly more toxic in the 14 day old rats [LD_{50} 3 ml/kg] than in adult rats [LD_{50} 6.4 ml/kg] and old adult rats [LD_{50} 7.4 ml/kg]. This is in contrast to benzene for which no significant difference in LD_{50} values was found in rats of different age, Kimura et al, 1971 (65).



13.3.4.14.4 SEX

No reports of differences in the response of animals to toluene based upon their sex were found.

13.3.4.14.5 SEASONAL VARIATIONS

No evidence of seasonal variations in toxicity were found.

13.3.4.14.6 NUTRITION

No studies in which the effect of nutrition on the toxicity of toluene was specifically studied were found.

13.3.4.14.7 HEALTH OF INDIVIDUALS

No studies of the state of health of animals and the effect of this on the toxicity of toluene were found.

13.3.4.14.8 INTERACTION WITH OTHER CHEMICALS

As mentioned in Section 13.3.3.3, when both toluene and benzene are given to rats at the same time, the toluene appears to interfere with the metabolism of benzene as demonstrated by a decrease in the expected amount of phenol excreted, phenol being a major metabolite of benzene but not of toluene. The toxicity of toluene is enhanced by exposure of rats to a mixture of perchloroethylene and toluene compared with exposure of rats to the same concentration of toluene alone. This effect of perchloroethylene is greater than would be predicted by a purely additive model for the toxicity of mixtures of perchloroethylene and toluene, Withey et al, 1975 (35).



13.3.5 HUMAN EXPERIENCE

Because toluene was thought for many years to have similar toxic effects on the bone marrow to those of benzene, toluene was suggested as a possible treatment for leukemia. It was found that leukemia patients tolerated daily doses of 10 g of toluene in olive oil for three weeks without complaints or clinical evidence of side effects (56).

Controlled 8 hour exposures of 3 humans twice per week to concentrations of 50, 100, 200, 300, 400, 600, and 800 ppm of toluene containing not more than 0.01 % benzene produced subjective complaints which were minimal at 50 and 100 ppm and consisted of moderate fatigue and mild headaches towards the end of the 8 hour exposure. At the exposure level of 200 ppm there was slight but definite impairment of co-ordination and reaction time. With higher concentrations, these effects became increasingly severe and at 600 ppm three hours of exposure resulted in extreme fatigue, mental confusion, exhilaration, nausea, headache and dizziness. At 300 ppm the normal 8 hour exposure period was cut to 3 hours because of extreme nausea, lack of self control, incoordination and staggering gait. No changes in white blood cells were noted over the entire four month period of these studies, Von Oettingen et al, 1942 (59). In an exposure of 2 male subjects to known concentrations of toluene for periods of 7-8 hours, it was found that the earliest central nervous system effects were found at 200 ppm. At this concentration a feeling of slight exhilaration was experienced. At 400 ppm lassitude, nausea and hilarity were noted. These symptoms became more marked at 600 ppm and at 800 ppm were characterized by transitory headaches, extreme lassitude, verbosity "inebriation" and nausea, Carpenter (16). The intensity of the



odor of toluene is a poor guide to the level of exposure due to the rapid blunting of the sense of smell due to the exposure. In the experiments of Von Oettingen et al (59) there was no irritation of the mucous membranes other than a slight smarting of the eyes and nose.

In experiments to determine the odor threshold and sensory threshold using 6 human volunteers, all of the subjects were able to detect the smell of toluene "concentrate" at a level of 16 ppm (0.064 mg/litre) and two were able to detect it at 1.6 ppm (0.0064 mg/litre). The toluene concentrate used in these experiments contained 46 % toluene, 0.06 % benzene with 46 % other aromatic hydrocarbons, Carpenter (62).

In 4 subjects exposed to 1 mg/m^3 (0.27 ppm) of toluene there was a distinct intensification of the electric potentials in the electroencephalogram from the left temporal occipital leads in all four subjects tested (56). This study by Gusev in the USSR raises the question of how to interpret such findings. The change in the electroencephalogram without any other abnormal finding could be interpreted as merely related to the olfactory perception of the presence of toluene or it could be interpreted, as it was by Gusev, as the first evidence of an adverse effect on human physiology. The problems associated with the interpretation of data, such as that from electroencephalograms, have not yet been resolved.

13.3.5.1 EPIDEMIOLOGICAL AND CLINICAL STUDIES

Because epidemiological studies involve information derived incidentally from persons exposed to toluene at work or in some other



situation, eg glue sniffing, there is little or no control over the "experimental" conditions. For this reason the comments made earlier with reference to the degree of purity of the toluene used in animal experiments should be borne in mind. In addition, few occupational exposures are confined to a single substance and over a period of time job and process changes render it most unlikely that substantial number of employees will be exposed to one compound of known composition for long periods at known and constant concentration. Despite all of these drawbacks, epidemiological studies continue to be important sources of information but this information must be carefully evaluated in the light of all of the information available from all sources in a search for consistent findings.

A further difficulty is introduced by clinical reports on exposures of individuals (cases of poisoning). Such cases may be very valuable in illuminating the toxicology of toluene, often at very high concentrations, but they may also involve unusual or unique personal conditions which make generalizations difficult or impossible.

13.3.5.2 HEMATOPOIETIC SYSTEM

Because of the chemical similarity of benzene and toluene, the known effects of benzene on the formed elements of the blood has caused toluene to also be considered as potentially having similar effects. This concern over the possible harmful effects of toluene on the hematopoietic system has been difficult to resolve because of the lack of availability of pure toluene prior to 1950. Human exposures prior to that date were



almost certainly to a mixture of toluene and benzene and even since that time documented exposures to pure toluene have been few.

In one of the few recorded therapeutic trials of toluene, the compound was given by mouth in daily doses of 10 g in olive oil as a possible treatment of leukemia. The treatments were given for three weeks without any side effects and no evidence of an effect on the circulating elements of the blood. The basis for this therapeutic trial was the belief that toluene, like benzene, was toxic to the bone marrow and might exert a beneficial effect in cases of leukemia (56).

In another study which focussed primarily on the possible effect of toluene on the blood and bone marrow, workers in a rotogravure plant, exposed for at least 3 years to printing inks containing toluene but no detectable benzene, were given extensive blood tests. These tests included five persons having examinations of bone marrow obtained by sternal biopsy. The hemoglobin, white and red cells and platelets were all within the normal range of values and did not differ significantly from the measurements made in a control population working in a part of the plant in which there was no exposure to toluene (57).

Similar negative findings were reported in 11 paint and pharmaceutical industry workers exposed to toluene in concentrations ranging from 200-800 ppm (56).

No evidence of an effect of toluene on the hematopoietic system was found in 17 workers who were exposed to a mean level of 125 ppm (range 8-300 ppm) while employed as labourers in a V-belt manufacturing plant.



Ethel Browning in her book "Toxicity and Metabolism of Industrial Solvents" (Elsivier Publishing Co., New York, 66-76, 1965) concludes from a review of the evidence available at that time that toluene has no toxic effect on the blood or blood-forming organs. No subsequent references have been found to suggest the need for an alteration of Browning's views.

13.3.5.3 NERVOUS SYSTEM

Reference has already been made to experimental studies in animals and humans which establish that, following slight smarting of the eyes, the earliest subjective effects of inhaled toluene are tiredness, mild headache and the onset of mental confusion. Pharmacologically, toluene acts as a narcotic but its side-effects are too great for it to have ever been used as an anesthetic. The results of the experiments of Von Oettingen are supported by the observation of a group of 1000 workers in industry who were exposed to toluene in three concentration ranges. In the range 50-200 ppm there were complaints of headache, lassitude and loss of appetite. In the range 200-300 ppm in addition to the other complaints there was slight incoordination, impaired reaction time and momentary loss of memory. In the exposure range 500-1500 ppm there were additional complaints of palpitations, extreme weakness and loss of coordination was pronounced. Although the subjective impressions in this study are generally in agreement with those of Von Oettingen, the purity of the toluene in the occupational exposure is not known (56).

An acute exposure to very high (10,000 ppm at waist level to 30,000



ppm at floor level) concentrations of toluene involving 29 men for unspecified exposure periods resulted in dizziness, "drunkenness", collapse and loss of consciousness. This episode resulted from the spraying of the hold of a ship with an insecticide using toluene as a vehicle. The purity of the toluene is not known, nor is the part played by the insecticide in the production of the symptoms, Longley et al, 1967 (66).

As with other compounds that can alter an individual's state of consciousness, toluene has been used for this purpose by persons seeking an escape from reality. The effects on the nervous system can range from rapidly reversible "inebriation" to permanent brain damage depending upon the length of the exposure period. In a man reported sniffing toluene several times a day for 14 years, a state of permanent incoordination, tremor and emotional lability developed. Physical examination showed permanent brain damage confirmed by electroencephalography and pneumoencephalography. While the level of exposure to toluene in this case can not be estimated it must have been exceedingly high. Evidence for the extreme level of exposure is provided by the information that the man purchased a gallon of pure toluene every four to six weeks to satisfy his addiction, Knox, 1966 (67). Not all cases of prolonged habituation to toluene result in such severe brain damage, but few can have been associated with such an intense exposure. In another case of habituation extending over a ten year period during which individual instances of intoxication resulted in headache, "inappropriate" speech and brief episodes of memory loss with occasional unconsciousness, no clinical or laboratory abnormalities were found other than excessive slow activity accompanied by sharp non-focal



discharges in the electroencephalograph, Satran et al, 1963 (68).

As the more severe occupational exposures are gradually brought under control, attention has tended to pass from the acute toxicological effects of toluene to the possible long term effects of lower levels of exposure. A further extension of this concern is the recognition that exposures in the "real-world" are seldom to only one chemical and therefore the possible interactions of chemicals at realistic levels of exposure are of increasing interest.

In a study, in Finland, of the long term effects of exposure to a mixture of organic solvents, 100 painters in an automobile repair shop were studied. The tests used included those for intelligence, memory, psychomotor performances and personality. The concentrations of the various solvents were low. Toluene was present in the greatest concentration in the mixture, with a mean concentration of 30.6 ppm (threshold limit value, 200 ppm) and the summated percentage concentration of the individual solvents amounted to only 31.8 % of the Finnish threshold limit value. The range of concentrations for the separate components was 4 to 212 % of the TLV. The possibility of higher concentrations having occurred in the past could not be ruled out.

The results of the tests in the solvent exposed group, when compared with a non-solvent exposed control group, showed impairment in



psychological performance as well as personality changes in the exposed group. Impairments in visual tests and verbal memory and a reduction of emotional reactivity were the central features of the adverse effects of solvent exposure.

These results are compatible with some hints in the literature that the effect of combined solvent exposure can be more hazardous than the summated effects of the components. The mean concentrations of the separate solvents was between 0.3 and 15.3 % of the corresponding TLV's and it seems unlikely that these concentrations would cause deleterious effects when occurring singly or even if their interaction caused a simple summated effect, Hanninen et al, 1976 (69).

13.3.5.4 RENAL EFFECTS

The so called hepato-renal syndrome has been reported to be a result of severe solvent exposure, but involvement of the kidney in toluene exposure has usually been slight or absent. There are, however, some reports that "sniffing" of toluene has been associated with Type 1 renal tubular acidosis and may be life threatening. In one of two such cases reported, the patient reported several episodes of muscle weakness following 4-7 days of solvent sniffing. One of these episodes required admission to hospital due to muscular weakness of all four limbs. Serum electrolytes showed a severe depression of potassium level (1.7 milliequivalents). Recovery was fairly rapid as the serum potassium level was restored to normal. Complete recovery, followed by relapses after further sniffing episodes, was recorded on several occasions, Taher et al, 1974 (70).



This acute and well documented effect of toluene on the renal tubule, with the consequent loss of potassium and the onset of muscular weakness, appears to be related to high levels of exposure to the solvent. A more troubling, but much less documented, renal disease due to solvent use is that of extracapillary glomerulonephritis. Although the number of cases reported is small, the long latent period between the beginning of exposure and the onset of disease makes the establishment of a cause and effect relationship difficult. All of the cases of glomerular kidney disease so far reported are due to mixed solvent exposures, no cases having been reported due to a pure toluene exposure.

13.3.5.5 GASTROINTESTINAL TRACT

Apart from the information that toluene is absorbed from the gastrointestinal tract, no local effects on the tract have been reported.

13.3.5.6 LIVER

In the reported harmful effects of toluene on the liver the toluene has always been of doubtful purity (56).

13.3.5.7 CARDIOVASCULAR

This subject is covered in Section 13.3.5.14.2.

13.3.5.8 RESPIRATORY SYSTEM

No reports of significant effects on the respiratory system have been found except those due to depression of the central nervous system with the consequent depression of respiration.



13.3.5.9 REPRODUCTIVE SYSTEM

No reports of an effect of toluene on reproduction were found.

13.3.5.10 ENDOCRINE SYSTEM

No reports of an effect of toluene on the endocrine system were found.

13.3.5.11 CARCINOGENICITY

No reports of a carcinogenic effect of toluene in humans was found.

13.3.5.12 MUTAGENICITY

Chromosome studies were carried out on peripheral blood lymphocytes of 24 workers of a rotogravure plant who had an exposure to toluene averaging close to the M.A.C. (200 ppm). The period of exposure varied from 3 to 15 years and there was no significant increase in the number of chromosome changes in the toluene exposed workers when compared with a healthy control population not exposed to toluene, Forni et al, 1971 (71).

13.3.5.13 TERATOGENICITY

No reports of toluene causing teratogenic effects in humans have been found.

13.3.5.14 FACTORS AFFECTING HUMAN RESPONSE

Very little information dealing with the factors which may affect human response to toluene have been found. One reason for this is, obviously, that studies in humans have almost always involved working populations which excludes the young and aged as well as seldom including



those with more than minor disabilities. For similar reasons, animal studies have not so far been concerned with reproduction, effects on the very young, etc., because the animal studies were carried out to provide information that could be extrapolated to adult working populations.

13.3.5.14.1 TOLERANCE

ODOR - The level of the threshold of detection of odor is heavily dependent upon the experimental method used, but is reported variously as 4.68 ppm for toluene derived from coke to 2.14 ppm for toluene derived from petroleum, Leonardos et al, 1969 (30). While other investigators have reported odor thresholds as high as 40 ppm, Dorigan et al (72), toluene shares a common property with odorous hydrocarbon solvents in that continuous exposure rapidly leads to dulling of the sensitivity of the olfactory sense organs, so that the ability to detect dangerous concentrations of the vapor is rapidly lost. In this rather restricted sense tolerance to the odor of toluene can be said to develop.

True tolerance, the ability to withstand levels of toluene that would cause unwanted effects in other persons or in the same person under other conditions, has not been reported but probably exists. The reason for this statement is that toluene is metabolized in the liver by means of hepatic side-chain hydroxylase and aromatic hydroxylase. These enzymes are inducible by such common drugs as phenobarbital which speed up the metabolism of toluene in animals. Similar effects could be expected to take place in man.



13.3.5.14.2 SUSCEPTIBILITY

Physical work, by increasing the ventilation of the lungs, increases the concentration of toluene in the blood. Experiments have shown that, during light work, the blood concentration of toluene was double that found at rest. At levels of toluene found in the blood during light work, at an atmospheric level of 200 ppm toluene, human subjects reaction time was impaired, Soderlund, 1975 (73).

Sudden death after inhaling toluene and other hydrocarbon solvents has been reported. Such deaths have been associated with sniffing toluene used as a solvent in airplane glue, Winek et al, 1968, 1971 (74, 75). By analogy with deaths from "sniffing" other hydrocarbon, chlorinated and fluorinated hydrocarbon solvents, the mechanism of death appears to be ventricular arrhythmias due to sensitization of the myocardium to a mixture of adrenaline and the solvent. The circumstances of "sniffing" are assumed to be associated with a state of excitement leading to adrenaline release.

13.3.5.14.3 AGE

No specific information on the effect of age on toluene toxicity was found.

13.3.5.14.4 SEX

No information on the effect of sex on toluene toxicity was found.

13.3.5.14.5 SEASONAL EFFECTS

No information on the effects of seasonal changes was found.



13.3.5.14.6 NUTRITION

No information on the effect of nutrition was found.

13.3.5.14.7 HEALTH OF INDIVIDUALS

No information on the effect of illness was found on the toxicity of toluene.

13.3.5.14.8 INTERACTION WITH OTHER CHEMICALS

Although several references deal with mixed exposures to benzene and toluene or other hydrocarbon solvents, in no case was there evidence of synergism or of antagonism. Usually the picture of toxicity was dominated by the compound with the highest toxicity, and this was usually benzene with which toluene is commonly contaminated unless a level of purity is specified.



13.4 XYLENE13.4.1 SUMMARY OF BIOLOGICAL INFORMATION

Irritant to nose and eyes at levels about 200 ppm. Onset of narcotic (central nervous system depression) effects at about 200 ppm.

Irreversible effects not reported at average present occupational levels (up to 100 ppm). Odor threshold about 1 ppm. Odor may cause complaints close to source.

Toxicity Rating: [C]

No irreversible effects at levels below 100 ppm in occupational exposure (40 hour week).

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	Low

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	Low
Epidemiological	Low

13.4.2 METABOLISM

All three isomers of xylene are metabolized in rabbits, rats and guinea pigs by oxidation of one of the methyl groups to the corresponding toluic acid. The second methyl group is resistant to oxidation, but in the animals mentioned a process of nuclear oxidation occurs in all three isomers of xylene by which urinary xylenols are produced as glucuronic conjugates (1).



Other studies have confirmed that the main metabolic pathway of all three isomers of xylene results in the formation of the corresponding toluic acid, which is then eliminated in the form of the hippuric acid conjugate. Approximately two to four percent of the absorbed dose of xylene is excreted in the form of xylenol and in no case was phthalic acid identified, confirming that the second methyl group resists oxidation, Bray et al, 1949 (76), Bakke et al, 1970 (77).

There are few studies of the metabolism of xylene in humans. In one such study, subjects were exposed in groups of four or five for seven hours, with a one-hour break after the third hour, to meta- or para-xylene at 100 ppm, or to meta-xylene at 200 ppm. These studies showed that 72 percent of the absorbed meta-xylene was excreted in the urine of male volunteers as meta-methylhippuric acid during and within 18 hours after the end of exposure. The results of this study showed that the total excretion of methylhippuric acid during and for 18 hours after exposure was the most accurate estimate of the level of xylene exposure, Ogata et al, 1970 (78). This investigation was done using pure meta- or para-xylene. Therefore, at this time there are no data available correlating urinary excretion with exposure to mixed xylene isomers. This single report of the metabolism of two isomers of xylene in man indicates that the major metabolic pathway for xylene involves oxidation of a single methyl group followed by conjugation with glycine or glucuronic acid.



13.4.2.1 ABSORPTION

Xylene is rapidly absorbed from the lungs, and in inhalation experiments with rats, the time in seconds of exposure to produce narcotic effects was uniformly greater for xylene than for toluene and benzene. The Starting concentration in each case was 15,000 parts per million (79). When given by mouth, xylene had greater acute oral toxicity to rats than either toluene or benzene, the LD_{50} for xylene being 4.3 g/kg while the LD_{50} for toluene and benzene was 7.0 and 5.6 g/kg respectively, Wolf et al, 1956 (28). These results are at variance with the LD_{50} intraperitoneal injection in mice, in which it was found that the LD_{50} for benzene was 1.15 ml/kg of body weight, for toluene 1.3 ml/kg of body weight and for xylene 1.8 ml/kg of body weight (79). One of the problems with all such estimates of toxicity is that the purity of the material is seldom stated and the relatively small differences noted could well be attributed to varying degrees of impurity.

13.4.2.2 DISTRIBUTION AND RETENTION

Apart from the metabolic information given above, no data on the distribution of xylene in animal tissues was found.

13.4.2.3 ELIMINATION

By analogy with the metabolism of benzene and toluene, it would seem reasonable that xylene also is excreted by the lungs, although no confirmation of this was found in the literature. The other major route of excretion is through the urine and the constituents found have been described above.



13.4.3 ANIMAL EXPERIMENTAL STUDIES

13.4.3.1 HEMATOPOIETIC SYSTEM

As in the case of toluene, experimental studies with xylene often present severe difficulties in interpretation due to lack of information about the purity of the solvent used. A further factor that must be considered in interpreting the effects of solvents in the hematopoietic system is that when solvents are injected, as they have been in many of the experiments, they produce a certain amount of tissue necrosis, which in turn leads to local inflammation and can result in changes in the number of white cells in the blood. If the earlier experiments using xylene of doubtful purity are discounted, there appears to be little evidence that xylene exerts a harmful effect upon the hematopoietic system. In a study using rats and rabbits exposed for eight hours a day, six days a week, to a benzene-free mixture of xylene isomers at two levels of exposure (5 mg/litre and 3 mg/litre), no significant changes in the blood were found at the lower concentration, while at the higher concentration there were decreases in both red and white cells. The duration of the high exposure study was 40 to 45 days and for the low level exposure, 110 to 130 days. At both concentrations of xylene, the bone marrow was hypoplastic but there was no tendency to aplasia, Fabre et al, 1960 (80).

In a later study, rabbits received xylene subcutaneously in doses of 30 mg/kg of body weight per day for six weeks, or 700 mg/kg of body weight for nine weeks. Full blood counts were made twice weekly, and



during the study all of the results fell within normal limits. Using tritiated methyl thymidine, it was found that xylene did not affect DNA synthesis in the bone marrow, although earlier, similar experiments with benzene had shown such a depression, Speck et al, 1968 (81)

In a series of reviews since 1943, the consensus has been that there is little evidence that xylene has a deleterious effect on the formed elements of the blood or of the bone marrow, Browning, 1950 (82), Lehmann and Flury, 1943 (83), Johnstone and Miller, 1960 (84).

13.4.3.2 NERVOUS SYSTEM

In studies described in 1960, the depressant effect of xylene was determined by measuring the threshold of excitability of the cerebral motor cortex before and after intraperitoneal injections of xylene.

In this series of experiments xylene was compared with benzene and toluene. Each of the solvents increased the excitation threshold but xylene showed the greatest increase. No changes followed the injection of physiological saline (79).

In studies in which rats were taught to avoid an electric shock by taking avoiding action at the sound of a buzzer, no effect of xylene in the range of 500 to 750 parts per million was found. The rats exposed to the xylene showed no difference in their response from those exposed only to air, either in acquiring the conditioned response or in losing the response if the buzzer was sounded but was not followed by an electric shock, Battig and Grandjean, 1964 (85).



In a study of the ability of rats to learn to run a maze, the naive rats were injected subcutaneously with either xylene or physiological saline at a dose of 0.05 millilitres per hundred grams of body weight. The difference between the test control groups was highly significant with the xylene treated animals taking longer to run the maze from the beginning and showing a slower learning rate. In similar experiments in which the animals had previously been trained to run the maze, the xylene treated group did not take significantly longer to complete the test than the control group, Desi et al, 1967 (86).

In a study of the behavioral effects of long term exposure to a mixture of organic solvents in 100 automobile painters compared with a non-exposed control group, the battery of tests used included those for intelligence, memory, psychomotor performance, and personality. The results indicated impairment in psychological performances as well as personality changes in the exposed group. Impairments in visual intelligence and verbal memory with some reduction of emotional reactivity were the central features of the adverse effects of solvent exposure, but the behavioral disturbances also involved several other functions including performance on a verbal intelligence test. The concentrations of the various solvents included in the exposure of the automobile painters was low, with the summated exposure corresponding to 32 % of the Finnish threshold limit value. The investigator concluded that there was toxicological evidence to support the conclusion that the effect of combined solvent exposure can be more hazardous than the summated effects



of the components. However, very little is known about the interaction of solvents such as xylene, toluene, alcohols, esters, ketones, and terpenes.

The investigators further postulated that the potentiated effect need not necessarily be potentiation in a toxicological sense. The impairment in automobile painters' performance could be the result of minor disturbances in several functions, caused by separate components of the exposure. Each one of these disturbances could perhaps be compensated for in the test situation as well as in everyday life when occurring alone, but when occurring together, complete compensation became impossible, Hanninen et al, 1976 (69).

13.4.3.3 RENAL SYSTEM

Except at high concentrations when xylene produces cloudy swelling of the kidneys of animals, no significant long-term effects of xylene upon the kidneys have been reported.

13.4.3.4 GASTROINTESTINAL TRACT

In most animal experiments using xylene, it has been given either by subcutaneous injection or by inhalation. In one of the few studies in which xylene was given by mouth to rats, it was found that the LD₅₀ for xylene was 4.3 grams per kilogram of body weight while the LD₅₀ for toluene and for benzene were 7.0 and 5.6 grams per kilogram of body weight respectively, Wolf et al, 1956 (28).



13.4.3.5 LIVER

Apart from slight necrosis of the liver at high levels of exposure, no significant effects of xylene exposure on the liver have been reported. The chemical changes undergone by xylene in the liver are described under the section on metabolism.

13.4.3.6 CARDIOVASCULAR SYSTEM

No reports of adverse effects of xylene upon the cardiovascular system were reported in animals, although, arguing by analogy with toluene and benzene, it would be expected that xylene can sensitize the heart to circulating catecholamines. However, no such reports were found in the literature.

13.4.3.7 RESPIRATORY SYSTEM

No reports of significant effects of xylene exposure upon the respiratory system were found.

13.4.3.8 REPRODUCTIVE SYSTEM

Pregnant white rats exposed to para-xylene vapor during gestation at a level of 500 mg of xylene per cubic metre (115 ppm) for 20 days, 24 hours a day, showed significantly greater pre-implantation mortality (32.1 %) than controls (11.3 %). Post-implantation mortality was also higher (38.9 %) for exposed animals, (4.8 % for control animals) (79). No other effects of xylene on the reproductive system or on reproduction have been found.



13.4.3.9 ENDOCRINE SYSTEM

No reports of the effect of xylene on the endocrine system have been found.

13.4.3.10 EYES AND OTHER SENSE ORGANS

Two drops of xylene instilled into rabbits' eyes produced slight conjunctival irritation with very slight and transient corneal injury.

Temporary corneal effects have also been reported with the formation of vacuoles in the corneas of cats exposed to xylene vapor. The vacuoles reportedly disappeared within a day when exposure to xylene was stopped. Similar changes have been reported in the eyes of furniture polishers exposed to xylene. In studies carried out in 1974, corneal vacuolization was not observed in the eyes of adult male New Zealand rabbits exposed to a mixture of xylene isomers. Xylene was instilled in the right eye of a rabbit once daily for two days and then three times daily on three days. Although the lids were swollen and partially denuded, the cornea appeared normal on fluorescein staining and on examination by hand slit-lamp and ophthalmoscope (79).

13.4.3.11 CARCINOGENICITY

If xylene were carcinogenic, one might expect that the effect would be similar to that shown by benzene in producing depression of the bone marrow with (in humans) later development of leukemia in some subjects. In the past, xylene was thought to have such significant deleterious effects on the bone marrow and the hematopoietic system in general but



more recent research casts doubt on these results, which in many cases were obtained with xylene of questionable purity. Recent better controlled studies give strong support to the conclusion that xylene uncontaminated by benzene has no harmful effects upon the bone marrow or formed elements of the blood. No animal studies suggesting that xylene is carcinogenic have been found.

13.4.3.12 MUTAGENICITY

No reports of mutagenic effects of xylene have been found.

13.4.3.13 TERATOGENICITY

In experiments in which chick embryos were exposed to unstated concentrations of xylene vapor for 60 to 240 minutes, a significant increase in malformations and mortalities was observed. These results correlated positively with the length of exposure to xylene. Younger chick embryos were more susceptible to the xylene effect (79). In the experiment previously referred to in which pregnant white rats were exposed to para-xylene during gestation, apart from the pre-implantation and post-implantation mortality, no teratogenic effects were observed.

13.4.3.14 FACTORS AFFECTING TOXICITY

13.4.3.14.1 TOLERANCE

No reports indicating the development of tolerance to the effects of xylene were found. However, it might be expected that by analogy with benzene and toluene, induction of microsomal enzymes would occur with xylene and its metabolic transformation thereby increased. No experimental verification of this speculation has been found.



13.4.3.14.2 SUSCEPTIBILITY

No reports of unusual susceptibility to xylene toxicity were found.

13.4.3.14.3 AGE

No reports of the effect of age on the response to xylene exposure were found.

13.4.3.14.4 SEX

No reports of differences in response to xylene based on the sex of the animals were found.

13.4.3.14.5 SEASONAL VARIATIONS

No reports of seasonal variations on the response to xylene exposure were found.

13.4.3.14.6 NUTRITION

No reports of the effect of differences in nutrition on the response to xylene exposure were found.

13.4.3.14.7 HEALTH OF THE INDIVIDUAL

No reports of the effect of the health of individual animals on their response to xylene exposure were found.

13.4.3.14.8 INTERACTIONS WITH OTHER CHEMICALS

No reports of synergistic or antagonistic toxic effects of xylene were found.



13.4.4 HUMAN EXPERIENCE

A number of experiments using human subjects have been carried out to establish the acute subjective response to xylene at various concentrations. In one such study, xylene at 200 ppm caused irritation of the eyes, nose and throat in a majority of the ten persons exposed. The subjects estimated that a concentration of 100 ppm would be tolerable for an 8 hour exposure. In contrast to these findings, toluene caused irritation of the eyes and throat in the majority of the subjects at 300 parts per million and they estimated that 200 parts per million would be tolerable for an 8 hour exposure.

In studies using six human subjects exposed for 10 seconds to a series of varying concentrations of xylene, it was calculated that the most probable odor threshold was about 4.5 milligrams per cubic metre or about 1 ppm (79).

In measurements of the ability of human subjects to detect aromatic hydrocarbons, 50 % of a trained odor test panel could just detect toluene at a concentration of 1.74 parts per million while the same panel could just detect xylene at a concentration of 0.27 parts per million, Hellman and Small, 1974 (87)

In studies of the effect of solvent vapors on the electrical activity of the cerebral cortex, four subjects were exposed to xylene at a concentration below the odor threshold. Xylene was reported to cause marked inhibition of electrical activity in contrast to benzene and toluene which were found to increase the electrical activity. The



threshold for these electrophysiological effects for xylene were 0.32 milligrams per cubic metre (0.07 parts per million). In view of the similar clinical effects of benzene, toluene and xylene on the central nervous system, these results appear paradoxical and require further validation (79).

There have been a number of case reports of persons exposed to relatively high concentrations of xylene vapor, usually mixed with other solvents, in which groups of workmen engaged in painting in confined spaces became dizzy, uncoordinated and, in the more severe exposures, unconscious. In almost all of these cases recovery was rapid upon removal from the exposure although several of the men were reported to have temporary impairment of renal and liver function. In only one of these cases was it possible to estimate the level of xylene exposure and this was in the worst case where one out of three men exposed at a level estimated to have been 10,000 parts per million, died as a result of his exposure.

13.4.4.1 EPIDEMIOLOGICAL STUDIES

No epidemiological studies have been reported in which the exposure was confined to xylene or where adequate comparisons with control populations had been made.

13.4.4.2 HEMATOPOIETIC SYSTEM

No epidemiological or case study reports have been found where hematological disorders could clearly be solely attributed to exposure to xylene. There are a handful of reports in which hematological



findings are described in persons exposed not only to xylene but to other solvents, often including benzene. In view of the animal data which suggests at this time that xylene is free of significant effect upon the hematopoietic system, there seems little reason to believe that human exposure to xylene is associated with deleterious effects on the bone marrow or on the formed elements of the blood.

13.4.4.3 NERVOUS SYSTEM

There is ample evidence from the epidemiological and case study reports that xylene is a central nervous system depressant, although there is almost no information about the levels of xylene exposure in such cases. Reference has already been made to the study of the behavioral effects of long-term solvent exposure in automobile painters exposed to a mixture of solvents including xylene, where the summated exposure level corresponded to 32 % of the Finnish threshold limit value. This report suggests that exposure to a mixture of solvents at less than their summated threshold limit value levels may have a more severe effect than would be predicted from their individual TLV's, Hanninen et al, 1976 (69).

13.4.4.4 RENAL SYSTEM

After undocumented but probably high exposure to xylene and other solvents, transient impairment of renal function has been reported as shown by a temporary steep rise in blood urea and a fall in endogenous creatinine clearance. In a review of the effect of solvents on the



kidney, it was considered that toluene and xylene were relatively free of effects upon the kidney unless the exposure to mixed solvents had been severe enough to cause significant liver damage, Enrenreich, 1977 (40).

13.4.4.5 GASTROINTESTINAL TRACT

One case is reported of a man mistakenly drinking a small amount of nitrocellulose varnish in which xylene was the main diluent. The man experienced immediate retrosternal burning, heat and redness of the face and some dyspnea. Tests later indicated toxic hepatitis with recovery in about three weeks, Browning, 1965 (37).

13.4.4.6 LIVER

In a number of instances where human exposure has been to mixed solvents, transient impairment of liver function has been reported. The case mentioned in the previous paragraph is one of the few cases where transient liver damage was reported from ingestion of paint thinner in which xylene was the predominant solvent.

13.4.4.7 CARDIOVASCULAR SYSTEM

No reports were found establishing an effect of xylene upon the cardiovascular system. By analogy with other aromatic solvents, it might be expected that exposure to xylene could sensitize the myocardium to circulating catecholamines but no reports of such cases were found in the literature.



13.4.4.8 RESPIRATORY SYSTEM

In the report previously referred to in which three painters were overcome by xylene vapor from the paint they were using in which the solvent was 90 % xylene, the man who died showed pulmonary edema and intra-alveolar hemorrhages. No other effects of xylene upon the respiratory system have been found apart from the irritation of the nose from inhalation at concentrations above the odor threshold.

13.4.4.9 REPRODUCTIVE SYSTEM

No reports of the effects on the reproductive system attributable to xylene exposure have been found.

13.4.4.10 ENDOCRINE SYSTEM

No reports of effects of xylene upon the endocrine system have been found.

13.4.4.11 EYES AND OTHER SENSE ORGANS

When six humans were exposed in turn to xylene, toluene, methyl acetate, ethylene acetate and butyl acetate evaporating from saturated filter paper, toluene was the most irritating to the eyes and xylene was the least irritating. In workers exposed to these solvents as furniture polishers, the workers suffered eye irritation and photophobia which was worst in the morning and gradually abated after a few hours of work. Careful examination of the eyes revealed minute vacuoles in the corneal epithelium. The cornea healed completely in a few days with no scars remaining even in workers who were frequently affected. The exposures were to mixed solvents including xylene and were of unknown concentration (79).



13.4.4.12 CARCINOGENICITY

No reports of neoplastic change attributed to xylene exposure were found.

13.4.4.13 MUTAGENICITY

No reports of mutagenicity due to xylene were found.

13.4.4.14 TERATOGENICITY

In a study of all human malformations recorded in Czechslovakia between the years 1959 and 1966, 20,000 malformations were found in 1,500,000 live and stillborn infants. Skeletal malformations included the caudal regression syndrome of nine of these infants. Five of the nine mothers involved had been exposed to fat solvents (xylene in one case) during their pregnancies. The investigator concluded that fat solvents, including xylene, may have a teratogenic effect causing caudal agenesis in man. This data, however, does not appear adequate to support such a conclusion (79).

13.4.4.15 FACTORS AFFECTING HUMAN RESPONSE

Although it can be assumed that a number of factors will affect the human response to xylene, no reports documenting such modified responses have been found.



13.5 NAPHTHALENE13.5.1 SUMMARY OF BIOLOGICAL INFORMATION

Eye and skin irritant. Lens opacity reported in 8 of 21 persons exposed to "high" levels. Cataracts found in rabbits dosed at "high" levels. No chronic effects reported at present levels of occupational exposure (average up to 10 ppm). At levels above 10 ppm, inhalation may cause headaches. Ingestion of high levels (moth balls) in children has caused hemolytic anemia.

Toxicity Rating: [B]

Data is scanty, acute toxicity appears low. Some suggestion of chronic effects on eyes and blood but recovery after ending exposure, exposure levels causing effects were probably "high".

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	Moderate

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	No Data
Epidemiological	Moderate (little data)

13.5.2 METABOLISM

Because little toxicological data was available on naphthalene, the standard format used in the majority of these documents has been abandoned in favor of a summary of the available information.



Naphthalene has a low acute toxicity with an LD₅₀ of 17.80 mg/kg of body weight in rats given naphthalene by mouth. The compound is relatively easily absorbed by mouth and in high concentrations has caused hemolytic anemia in dogs which recovered rapidly when the administration of naphthalene was stopped. After absorption, the naphthalene is believed to be oxidized to alpha-Naphthol, which is excreted in the urine as naphthyl glucuronate and ethereal sulfate

Cataracts of the eye resembling human senile cataracts have been found in rabbits repeatedly given naphthalene (1 g/kg) for periods up to 28 days. Damage to the eyes of young rabbits has also been reported when the mothers were exposed to naphthalene, although the mothers, themselves, suffered no apparent injury, Heyningen, 1976 (88).

Naphthalene is believed to be readily absorbed from the respiratory tract, but no information is available concerning skin absorption.

In humans, the most common toxic effect of naphthalene is dermatitis and individuals vary considerably in their sensitivity to this effect of naphthalene. The skin rash usually clears up rapidly upon discontinuation of the naphthalene exposure.

The compound will cause irritation when it comes in contact with the eyes, but no serious eye injuries have been reported in humans.

Inhalation of naphthalene vapor has been reported to cause headaches, confusion, nausea and profuse perspiration. Little or no information is available in the literature concerning the exposure levels that produce these effects.



Ingestion of naphthalene has not been unusual in the past in children due to the widespread availability of mothballs made of naphthalene. The usual symptoms were nausea, vomiting and diarrhea, while hemoglobinuria, anemia, and a raised white count were the chief observations. The reactions resembled those seen in Sickle Cell anemia during a hemolytic crisis, but there was no evidence of sickling. The patients recovered promptly, although in some cases blood transfusion was necessary because of the anemia. No substantiated chronic toxic effects have been reported as a result of industrial exposure to naphthalene and an occupational exposure limit of 10 parts per million (50 mg/cubic metre) has been established by the American Conference of Governmental Industrial Hygienists. 8 cases of opacity of the lens of the eye have been reported among 21 persons exposed for 5 years to "high" concentrations of naphthalene (89).

Despite the close chemical relationship between naphthalene and 1-naphthylamine, a potent bladder carcinogen, naphthalene, itself, has not been shown to be carcinogenic or mutagenic (90). The lack of carcinogenic activity for naphthalene is of interest in comparing its metabolism with that of benzene. The ability of benzene to cause aplastic anemia and leukemia (in man) has been postulated to occur because of the production of 1,2-benzene oxide. This highly reactive and unstable compound is quickly converted to phenol by non-enzymic isomerization of 1,2-benzene oxide, Gibson et al, 1968 (91). As discussed in the section on metabolism of benzene, the oxide has not been isolated in vivo but, when liver homogenate is incubated with benzene oxide, the normal



metabolites of benzene are formed thus supporting the theory that benzene oxide is an intermediate step in the metabolism of benzene.

It is of interest that a similar metabolic pathway can be demonstrated for naphthalene but no carcinogenic or mutagenic activity is associated with these reactions.

1,2-naphthalene oxide has been demonstrated after incubation of naphthalene with liver homogenates. The naphthalene oxide was then converted to naphthols by non-enzymic isomerization of the oxide, Jerina et al, 1969 (92). It has been suggested that these results may mean that some structural property in addition to dihydrodiol epoxide structure must be essential for a polycyclic hydrocarbon to be carcinogenic.



13.6 CUMENE13.6.1 SUMMARY OF BIOLOGICAL INFORMATION

Skin irritant and central nervous system depressant. No human poisoning reported. Acute toxicity higher than benzene and toluene. Slow elimination from animals suggests possibility of cumulative effects.

Toxicity Rating: [C]

Rating [C]. Occupational exposure limit 50 ppm (TWA).

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Moderate
Chronic	No Data

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	No Data
Epidemiological	No Data

13.6.2 METABOLISM

There is very little literature on the toxicology of mono-isopropylbenzene (Cumene). For this reason, the format used in the other sections of this chapter will not be used.

No cases of human poisoning from acute exposure to cumene have been reported and all toxicological information derives from animals experiments. In animals, cumene has been found to be less toxic than benzene or toluene, the lethal intraperitoneal dose in guinea pigs being found to be 1.3 gm/kg of body weight, while the respective doses



for benzene and toluene were 0.65 and 0.41 gm/kg of body weight respectively (1).

The effect of cumene is principally that of a central nervous system depressant with a pharmacologically narcotic effect, but there is some contradiction in the literature as to whether the inhalation of cumene is more toxic than the inhalation of benzene or toluene. Lazarew, 1929 (93), using white mice, found that a concentration of 20 mg cumene/l of air caused prostration, while 25 mg cumene/l of air produced a loss of reflexes. Benzene caused similar prostration at levels of 15 mg/l, and toluene at 10-12 mg/l.

In contrast, Werner et al, 1944 (94), found the lethal concentration of cumene for mice to be 10 mg/l, and that of toluene and benzene to be 19.9 and 33.1 mg/l respectively, thus these workers found a greater acute toxicity for cumene than for benzene and toluene. However, they also found that the narcotic effect, while occurring much more slowly in the case of benzene and toluene, once established was very much more persistent.

Dogs given cumene showed a rise in the urinary excretion of sulfoconjugates which suggests the intermediate production of phenol compounds (1). Later investigators showed that the administration of cumene to rabbits produced urinary glucuronic conjugates, Robinson et al, 1955 (95).

No information on the metabolic fate of cumene in man was found. In a study of the chronic toxicity of cumene, rats and rabbits were exposed to concentrations of 6.5 to 12 mg/l, for 7 hrs/day, 6 days/week for a period of 130 to 180 days. During the course of this study



repeated hematological examinations were carried out and no abnormalities were detected. At the end of the experiment, no effect of cumene on the bone marrow was found, and apart from slight passive congestion, no abnormalities were discovered in the tissues, with the exception of the kidneys where some renal changes were found similar to those reported in the case of toluene (1).

As with other similar solvents, cumene is a primary skin irritant which is partly absorbed through the intact skin. The relatively slow elimination of cumene suggests that long exposures may result in cumulative effects. The American Conference of Governmental Industrial Hygienists has established a threshold limit value of 50 parts per million for cumene (245 mg/cubic metre).

On the somewhat scanty information available, it would appear that cumene is a central nervous system depressant, but devoid of bone marrow toxicity or carcinogenicity in the limited tests so far carried out. Cumene is also irritating to the eyes, skin and upper respiratory tract.



13.7 STYRENE13.7.1 SUMMARY OF BIOLOGICAL INFORMATION

Skin and eye irritant, changes in EEG reported at average exposure of 30 ppm. Central nervous system depressant. Some reduction in pulmonary function in chronically exposed workers, styrene shown to be mutagenic and therefore a suspected carcinogen. Odor threshold is 0.1 ppm. Occupational exposure limit TWA 100 ppm.

Toxicity Rating: [A]

Given rating of [A] on basis of suspected carcinogen due to mutagenicity. No human studies confirm carcinogenicity, but no long term studies are reported. At low concentrations odor produces complaints.

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	Moderate

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	Moderate
Epidemiological	Moderate

13.7.2 METABOLISM

Styrene is metabolized in animals and in man to hippuric acid, which is excreted in the urine. The metabolic routes of styrene are fairly well known and are similar in many species of animal. The first step is thought to be the formation of styrene oxide, which is subsequently hydrated to styrene glycol or conjugated with glutathione.



Styrene glycol may be further conjugated with glucuronic acid or converted to mandelic acid, which in turn is oxidized to phenylglyoxylic acid or benzoic acid. It is this latter acid which is conjugated with glycine to give the hippuric acid mentioned earlier, Parkki et al, 1976 (96).

Partly because styrene is structurally similar to vinyl chloride and partly because styrene is metabolized to styrene oxide, there has been considerable interest in the possible carcinogenicity and mutagenicity of styrene. This is dealt with under Section 13.7.3.11 CARCINOGENICITY.

In a study comparing the uptake and distribution of methyl chloroform, toluene and styrene, it was found that the initial alveolar concentration of styrene was the smallest of the three compounds in proportion to the exposure level and it increased the least with increased ventilation. The arterial concentration of styrene increased throughout the entire period of constant exposure while during this time the alveolar concentration remained the same.

If the transfer of styrene from arterial blood to other organs was as rapid as the uptake of fresh solvent into the arterial blood per unit of time, the blood concentration should not rise. Thus the solubility in other tissues appears to be lower than in blood, unless the total uptake capacity is low. These findings are in contrast to those found with methyl chloroform, which is relatively insoluble in blood, whereas toluene is intermediate in solubility in blood between



methyl chloroform and styrene. These experiments were conducted in two human subjects exposed to 50, 150, 250 and 350 parts per million of styrene in the inspired air at rest. The duration of exposure was 30 minutes at each concentration. The mandelic acid concentration in the urine was measured after each exposure and the maximal mandelic acid concentration was found 3 to 5 hours after the end of the exposure. This level did not return to the base line values until about 9 to 13 hours following the exposure. One of the practical conclusions of this study is that alveolar styrene concentrations are poorly correlated with the concentration of styrene in the inspired air, but the venous blood concentration of styrene closely followed the concentration of the solvent in the arterial blood, of course, this type of sampling is difficult to perform in a working environment. Further studies showed, however, that there was very good agreement between the concentration of styrene in arterial blood and arterialized capillary blood. Therefore, a measurement of the concentration of styrene in the capillary blood obtained from a fingertip sample can be used as a method of measuring human styrene exposure.

The possibility of using mandelic acid in the urine as an index of styrene exposure was explored, but at low levels of styrene exposure the variability of mandelic acid concentration in the urine was too great to provide a reliable index of exposure. The biological limit values suggested for mandelic acid have been set at 1.5 to 1 gm/l of urine. These values correspond approximately to 50 parts per million of styrene during an 8 hour working day, Astrand et al, 1974 (97).



In a study of 17 men exposed to styrene in 4 workshops using fiber glass resin, it was found that in general the time-weighted styrene exposure could be estimated from measurements of mandelic acid in the urine taken at the end of the work day. These investigators found that an exposure to 50 parts per million of styrene gave a level of approximately 1,000 parts per million of mandelic acid in the urine and an exposure to 100 parts per million of styrene gave a mandelic acid level of 2,000 parts per million. Some caution would seem in order, however, in interpreting urinary mandelic acid levels in terms of styrene exposure since a sub-group of the workers studied in this investigation showed a negative correlation between the mandelic acid concentration in the urine and the styrene concentration in the air. This paradoxical finding was not explained, but would mean that a wrong conclusion might be drawn from merely analyzing the urine for mandelic acid, rather than also measuring the actual styrene level in the inspired air, Gotell et al, 1972 (98).

The metabolism of styrene takes place principally in the liver and is stimulated by phenobarbital and reduced by simultaneous exposure to toluene, Ikeda et al, 1972 (99).

About 1 % of the absorbed styrene is excreted in the expired air in man, the rest being metabolized to a mixture of hippuric, phenyl glyoxylic, and mandelic acids, which are excreted in the urine.

13.7.2.1 ABSORPTION

Styrene is readily absorbed from the lungs as has been mentioned under the section on Metabolism.



No information on the absorption of styrene from the gut was found, but there is some evidence that it is absorbed slowly through the skin, Heine et al, (100).

13.7.2.2 DISTRIBUTION AND RETENTION

No detailed information on the distribution of styrene within the body after absorption has been found beyond that referred to under the section on Metabolism.

13.7.2.3 ELIMINATION

Only about 1 % of the absorbed styrene is eliminated through the lungs in man, the rest being metabolized and excreted in the urine with the metabolites reaching a peak between 3 to 5 hours after the cessation of the exposure. In experimental studies in humans, equilibrium was not reached between the blood concentrations of styrene and the level of styrene in the inspired air within the 30 minute period of the experiment, Astrand et al, (97).

13.7.3 ANIMAL EXPERIMENTAL STUDIES

13.7.3.1 HEMATOPOIETIC SYSTEM

No evidence of significant effects of styrene on the blood or the blood forming organs has been found in the Western literature, Zeilhuis 1962 (101), although Eastern European authors regard the toxicity of styrene as serious, finding abnormalities in the central nervous system, hematological system and liver, Zlobina, 1971 (102).



13.7.3.2 NERVOUS SYSTEM

Styrene is a central nervous system depressant although, at exposures of 1,300 parts per million, a small proportion of rats and all guinea pigs died after 40 hours of continuous exposure due to pulmonary edema, Spencer, 1942 (103).

A 1.5 gm/kg of body weight dose of styrene did not cause any visible effects in rats, but styrene oxide was more toxic and the maximum tolerable dose of this compound was found to be 375 mg/kg of body weight. When styrene glycol was given, the tolerable limit was doubled to 750 mg/kg of body weight. All of these doses were given by intraperitoneal injection. At the maximum tolerated dose, the compounds acted as anesthetics, the animals being sleepy for a period of about 3 to 4 hours after the injections. It appeared that it was probable, therefore, that the anesthetic effect of styrene may be due in part to its metabolite styrene glycol (96).

13.7.3.3 RENAL SYSTEM

Only one vague reference to kidney damage was found in a report of rats exposed to 1,300 parts per million of styrene 8 hours daily, 5 days a week for 6 months, Leibman, 1975 (104).

13.7.3.4 GASTROINTESTINAL TRACT

No information on effects of styrene on the gastrointestinal tract were found.



13.7.3.5 LIVER

As has been reviewed under the heading Metabolism, styrene is mainly metabolized in the liver and styrene is capable of inducing liver microsomal enzymes. However, no other significant effects of styrene upon the liver have been found (104).

13.7.3.6 CARDIOVASCULAR SYSTEM

No adverse effects of styrene on the cardiovascular system have been found.

13.7.3.7 RESPIRATORY SYSTEM

In the study referred to above (104), 10 % of the guinea pigs exposed at 1,300 parts per million for 8 hours a day, died within a few days of "pulmonary irritation".

13.7.3.8 REPRODUCTIVE SYSTEM

No report of the effect of styrene on the reproductive system was found.

13.7.3.9 ENDOCRINE SYSTEM

No information on the effect of styrene on the endocrine system was found.

13.7.3.10 EYES AND OTHER SENSE ORGANS

Eyes and nose irritation was common in animals exposed to 1,300 parts per million of styrene and was present at 650 parts per million styrene (104).



13.7.3.11 CARCINOGENICITY

Forty 12 week old C_3H mice were painted on the clipped dorsal skin with a 5 % solution of styrene oxide in acetone thrice weekly for life. No skin tumours were observed in 33 animals that survived 17-24 months. Forty C_3H mice were similarly painted with a 10 % solution of styrene oxide in acetone; only 2 mice survived at 17 months, and no tumors were observed, Weil et al, 1963 (105).

Of 30 8-week old male Swiss ICR/Ha mice given thrice weekly applications of 0.1 ml of a 10 % solution of styrene oxide in benzene on the clipped dorsal skin for life, 3 developed skin tumors; one of these had a squamous-cell carcinoma. The median survival time was 431 days. Of 150 benzene-painted controls, 11 developed skin tumors, and one of these had a squamous-cell carcinoma, Van Duren et al, 1963 (106).

No reports of long term animal feeding studies upon which to base a judgement as to the carcinogenicity of styrene have been found.

13.7.3.12 MUTAGENICITY

Because of the wide use of styrene and its resemblance to vinyl chloride, the mutagenic potential of styrene and its metabolites in bacterial systems has been studied by a number of workers. It seems clear that the metabolite styrene oxide is mutagenic to *Salmonella Typhi-murium* that have been especially altered to detect mutagens. Specifically, strains TA-1535 and TA-100 have been used and styrene oxide has been shown to cause base-pair substitutions under these circumstances. Styrene oxide seems to be a directly acting mutagen, because the



presence of an enzyme preparation does not enhance its mutagenicity, Vainio et al, 1976 (107). Although styrene is fairly toxic to Salmonella, there appears to be some evidence that styrene is directly mutagenic in the TA-100 strain.

In the presence of liver homogenate, styrene appears to be more mutagenic to strain TA-1535 than styrene oxide.

Styrene itself was found to be inactive in the production of forward mutations in yeast, even in the presence of purified mouse liver microsomes. Styrene oxide was active in forward mutation experiments with both yeast and Chinese hamster cells.

Since it is considered that epoxides produced as metabolites of carcinogenic aromatic or olefinic compounds may be responsible for their mutagenicity and carcinogenicity, the finding of mutagenic activity caused by styrene oxide suggests that exposure to styrene vapor itself may be harmful owing to its metabolic conversion to styrene oxide. Although styrene oxide can be considered a potent mutagen in the production of forward mutations in mammalian somatic cells in culture, it is worth remembering that the mutagenic effect observed by styrene in vivo was only obtained with very high doses (1,000 mg/kg of body weight), Loprieno et al, 1976 (108).

13.7.3.13 TERATOGENICITY

No reports of teratogenicity have been found.

13.7.3.14 FACTORS AFFECTING TOXICITY

13.7.3.14.1 TOLERANCE

No reports were found suggesting the development of tolerance in



experimental animals.

13.7.3.14.2 SUSCEPTIBILITY

No reports were found dealing with special susceptibility to styrene in any experimental animals.

13.7.3.14.3 AGE

No reports on the effects of age on the toxicity of styrene were found.

13.7.3.14.4 SEX

No reports on the effects of sex on styrene toxicity were found.

13.7.3.14.5 SEASONAL VARIATIONS

No reports suggesting a seasonal effect on toxicity were found.

13.7.3.14.6 NUTRITION

No reports were found that were relevant to the effect of nutrition on the toxicity of styrene.

13.7.3.14.7 HEALTH OF INDIVIDUAL

No reports on the effect of health on the toxicity of styrene were found.

13.7.3.14.8 INTERACTION WITH OTHER CHEMICALS

No reports of the modification of the toxicity of styrene by its interaction with other chemicals to which the animals might be exposed were found.



13.7.4 HUMAN EXPERIENCE

13.7.4.1 EPIDEMIOLOGICAL AND CLINICAL STUDIES

In a cross-sectional study of the health of 17 men working in four factories all engaged in the manufacture of plastics reinforced with fibre glass compared with the health of a control group not so exposed, the following findings were reported. Complaints of irritation of the eyes and throat characteristic of high styrene exposures were common (114 and 263 parts per million average for the medium and high exposure groups respectively). The concentrations of styrene causing complaints of irritation appear to vary greatly from individual to individual. Tolerance may increase with time, or persons with undue sensitivity to styrene may leave these occupations since it was found that the investigators could not stand concentrations of 500 to 800 parts per million for more than one to two minutes, although the workers exposed to this intensity for hours often complained of only minor or moderate irritation. All subjects had a full medical history taken and a simplified neurological examination was carried out. In addition, lung function studies were performed and measurements of simple reaction time were carried out before and after work.

When compared with the age-matched controls, the exposed group showed significantly longer reaction times in the morning but not in the afternoon. When this result was further examined, it was found that the group of four subjects exposed to more than 150 parts per million were responsible for all the abnormal reactions, and this subgroup had significantly prolonged reaction times both in the morning and the afternoon when compared with their age-matched controls. The authors of



the study felt that a time-weighted average of 50 parts per million would be a safe level of exposure under the conditions tested, and that the ceiling level, which should not be exceeded, should not be greater than 300 to 400 parts per million, since at that level the unadapted observers suffered from lachrymation and irritation of the throat. In this study the lung function tests showed no evidence of abnormality, Gotell et al, 1972 (98).

In a study of the literature, Zielhuis, 1962 (101) found that irritation of the eyes and throat and non-specific tiredness were commonly associated with industrial exposure to styrene. Hematological abnormalities were generally minimal or absent, but the author notes that in East European countries the toxicity of styrene is regarded as serious, with reports of abnormalities of the central nervous system, liver and hematological system.

In a study of 494 workers exposed to styrene, 98 percent of whom were male with a median age of 40 years, no unusual clinical patterns were found, although the possibility that styrene may have a significant effect on the lower respiratory tract was suggested by the fact that 30 percent of the non-smokers had reductions in pulmonary function and 12 percent of the highly exposed workers (compared to 4 percent of the group having a lower exposure) had repeated episodes of wheezing and/or tightness in the chest, suggesting a causative relationship. There was no suggestion of an effect on the blood or the blood-forming organs. Exposures in this study were based on job descriptions and actual tasks performed; no measurements of styrene concentrations are given. Men were grouped into "high" and "low" exposure groups. Lorimer et al, 1976 (109).



13.7.4.2 HEMATOPOIETIC SYSTEM

In the epidemiological and clinical studies reported, no significant effect of styrene on the hematopoietic system has been found.

13.7.4.3 NERVOUS SYSTEM

Styrene is a central nervous system depressant and at high levels causes incoordination symptoms described by the individual as light-headedness or drunkenness. In a study of 98 male workers employed in the manufacture of reinforced polyester plastic products in which the polyester resin was spread by hand, the results of a battery of psychological tests were compared with those of 43 male workers producing reinforced concrete products. The comparison between the exposed and non-exposed workers revealed very few statistically significant differences. The psychological functions studied were intelligence, visuomotor speed, visuomotor accuracy, memory, vigilance, and psychomotor performance. The styrene-exposed group had significantly poorer visuomotor accuracy and poorer psychomotor performance. These results were confirmed when the workers with low and high styrene exposure were compared.

The exposure to styrene was measured by the level of excretion of mandelic acid. Those with a mean mandelic acid concentration of less than 674 mg per litre were considered to have a low exposure (this level of mandelic acid concentration corresponds to about 25 parts per million time-weighted average concentration of styrene) while those with a mean mandelic acid concentration of more than 1762 mg per litre



were considered to have a high exposure (this urinary mandelic acid concentration corresponding to about 75 parts per million time-weighted average of styrene exposure).

The correlation between mandelic acid concentration and disturbances in psychological function yielded some evidence of a dose-response relationship, but this effect was confounded by the variable durations of the styrene exposure and the possibility of selection occurring among the workers, Lindstrom et al, 1976 (110).

13.7.4.4 RENAL SYSTEM

No reports of adverse effects of styrene on the renal system were found.

13.7.4.5 GASTROINTESTINAL TRACT

No reports of adverse effects of styrene upon the gastrointestinal tract were found.

13.7.4.6 LIVER

In the epidemiological study referred to earlier (114), hepatic function was investigated by measuring bilirubin, alkaline phosphatase, SGPT, GGTP and SGOT. The only significant differences found in liver function tests between the high and low styrene exposed groups were in the GGTP measurement, 6.7 percent of those in high styrene exposure having an elevated level while only 2.8 percent in the low styrene exposure group had such a finding.



No other reports of liver abnormalities due to styrene exposure were found.

13.7.4.7 CARDIOVASCULAR SYSTEM

No reports of cardiovascular abnormalities due to styrene exposure were found.

13.7.4.8 RESPIRATORY SYSTEM

The study by Lorimer (105) showed, as mentioned above, that significantly more high than low exposed workers had complaints of wheezing or tightness in the chest, which the workers attributed to styrene exposure. In pulmonary function measurements of airway obstruction, 31.6 percent had evidence of airway obstruction although no simple dose-response relationship could be found.

13.7.4.9 REPRODUCTIVE SYSTEM

No reports of effects on the reproductive system were found.

13.7.4.10 ENDOCRINE SYSTEM

No reports of effects of styrene exposure on the endocrine system were found.

13.7.4.11 EYES AND OTHER SENSE ORGANS

Exposure to styrene vapor may cause eye and nasal irritation. The odor threshold is reported to be 0.1 parts per million for the inhibited material and 0.047 parts per million for the uninhibited, Leonardos et al, 1969 (30).



13.7.4.12 CARCINOGENICITY

No reports of human carcinogenicity due to styrene have been found.

13.7.4.13 MUTAGENICITY

No reports of mutagenicity in humans exposed to styrene were found.

13.7.4.14 TERATOGENICITY

No reports of teratogenicity in humans exposed to styrene were found.

13.7.4.15 FACTORS AFFECTING HUMAN RESPONSE13.7.4.15.1 TOLERANCE

Apart from the much greater tolerance of the irritant effects of styrene reported above, no other evidence of significant tolerance to the effects of styrene have been found.

13.7.4.15.2 SUSCEPTIBILITY

No particularly susceptible groups have been reported, although it seems possible that persons finding styrene particularly irritating might be expected to leave occupations in which they were exposed to styrene.

13.7.4.15.3 AGE

No reports of age-related responses to styrene were found.



13.7.4.15.4 SEX

No reports of differences of response to styrene in the sexes have been found.

13.7.4.15.5 SEASONAL EFFECTS

No reports of seasonal effects of styrene exposure have been found.

13.7.4.15.6 NUTRITION

No reports of the effect of nutrition on styrene exposure have been found.

13.7.4.15.7 HEALTH OF THE INDIVIDUAL

No reports of the effect of previous health status on styrene exposure have been found.

13.7.4.15.8 INTERACTION WITH OTHER CHEMICALS

No reports of the effect of combined exposures of styrene with other chemicals have been found.



13.8 ETHYLBENZENE13.8.1 SUMMARY OF BIOLOGICAL INFORMATION

Skin irritant and central nervous system depressant. Very little data is available but no evidence of chronic effects from occupational exposure. Occupational exposure limit TWA 100 ppm.

Toxicity Rating: [C]

Toxicity to Animals

<u>Test</u>	<u>Rating</u>
Acute	Low
Chronic	No Data

Toxicity to Man

<u>Test</u>	<u>Rating</u>
Experimental	No Data
Epidemiological	No Data

13.8.2 INTRODUCTION

Because of the paucity of data on the human and animal toxicity of this compound, the format used in the other reports will be abandoned in favor of a short summary of the available information.

13.8.3 METABOLISM

The main oxidation of ethylbenzene occurs at the activated alpha-methylene group to yield methylphenylcarbinol which is also the precursor of hippuric and mandelic acids. Both optical isomers of methylphenylcarbinol are formed, probably in equal amounts, and these have been isolated from the urine of rabbits as the corresponding glucuronides. The two optical forms of mandelic acid have also been found, Williams, 1959 (111).



13.8.4 ACUTE TOXICITY

The acute oral LD₅₀ value in rats was reported as 5.46 millilitres per kilogram of body weight, Smythe et al, 1962 (112). The dermal LD₅₀ value in rabbits is reported as greater than 5 grams per kilogram of body weight, although ethylbenzene produced only moderate irritation when applied full strength to intact or abraded rabbit skin for 24 hours under an occlusive dressing. In sensitization tests in humans using a concentration of 10 % ethylbenzene in Petrolatum, no sensitization reactions were found.

13.8.5 SKIN PENETRATION

Ethylbenzene has been found to be well absorbed through the skin of rats.

13.8.6 HUMAN EXPERIENCE

Experimental exposure of six men showed that a concentration of 1000 parts per million was irritating to the eyes, but that irritation decreased on continued exposure, until after a minute or two it was scarcely noticeable; at 2,000 parts per million one observer stayed in the atmosphere 5 minutes and found that irritation to the eyes and throat gradually disappeared but that vertigo developed, Gerarde , 1963 (113).



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	SECTION	PAGE NO.
14	STANDARDS	14-1
14.1	SUMMARY	14-3
14.2	OCCUPATIONAL HEALTH STANDARDS	14-5
14.3	AMBIENT AIR STANDARDS	14-10
14.4	WATER STANDARDS	14-12
14.5	REFERENCES	14-13



14.1 SUMMARY

In Ontario the occupational standards for the aromatic compounds of interest here are based on eight hour average concentrations and are the same as the TLVs recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). Current standards are listed as:

- benzene	10 (32) ppm (mg.m^{-3})
- toluene	100 (375)
- xylene (o-,m-,p-)	100 (375)
- ethylbenzene	100 (375)
- cumene	50 (245)
- styrene	100 (420)
- naphthalene	10 (50)

The Ontario standards are identical to the recommended TLVs of the ACGIH and, with the exception of benzene, to TWAs set by OSHA in the U.S. In the U.S. the TWA for benzene is currently 1 ppm or 3 mg.m^{-3} with a ceiling of 5 ppm or 16 mg.m^{-3} . Enforcement of this lower level for benzene has been temporarily restrained pending the outcome of a federal appeal court decision.

In Ontario, ambient air standards, which refer to a half hour average point of impingement concentration, have been promulgated for most of the compounds of interest here. The regulations are:

- benzene	10.0 mg.m^{-3}
- toluene	2.0
- xylenes	2.3



- ethylbenzene 4.0
- styrene 0.40

Water quality standards currently in force generally use such parameters as COD, BOD, TOC, turbidity, fish toxicity, etc. No standards specific for the aromatic compounds of interest here were found.



14.2 OCCUPATIONAL HEALTH STANDARDS

Occupational health standards are variously referred to as "Threshold Limit Values" (TLVs), "Time Weighted Averages" (TWAs), "Short Term Exposure Limits" (STELs), "Maximum Allowable Concentrations" (MACs), "Maximum Permissible Concentration (MPCs), etc. depending on the organization issuing the standard or the jurisdiction within which the standard is applied.

In the U.S. there are three organizations which publish standards for sets of compounds. These are the Occupational Safety and Health Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH) and the American National Standards Institute (ANSI). Standards set by ACGIH are guidelines, updated annually, for occupational exposures. However, OSHA sets occupational standards under mandate of the U.S. Occupational Safety and Health Act (1970) and such standards thus become part of the U.S. law.

OSHA standards are expressed as "Time Weighted Average" (TWA) concentrations, which represent the average concentration of a compound usually over an 8 hour working day. TWAs are chosen for which almost all workers may be repeatedly exposed, on a long term daily basis, without adverse effects. Notwithstanding TWA requirements, there are often also prescribed "ceiling" levels which are higher concentrations than the TWAs and represent concentrations which may not (except under certain conditions) be exceeded, even for short periods of time. For those compounds for which no ceiling level is given, excursion factors are applied (based on the TWA) which effectively determines ceiling levels. The ceiling levels may be exceeded only where higher peak levels are allowed. These higher levels are usually limited to a certain concentration which may occur for no more than a defined



period of time and a maximum frequency during a working day. For example, the OSHA listed TWA for styrene is 100 ppm (8 hour average) and the ceiling is 200 ppm. This ceiling of 200 ppm may only be exceeded once every three hours, for a duration of no more than five minutes on each occasion and only up to a maximum concentration of 600 ppm.

In addition to the above, OSHA also defines an "action level" as one half of the TWA. Once 8 hour average concentrations reach this "action level", certain monitoring activities are required. It may also be required that additional control measures or other actions be taken, in anticipation of exposures above the TWA, in order to protect workers against such exposure.

The ACGIH defines maximum exposure limits above ceiling levels as "Short Term Exposure Limits", (STEL). These represent the maximum concentration which may occur at any time and such concentrations are limited to a maximum period of 15 minutes. There must be at least 60 minutes between such excursions and no more than four in a given work day.

In Canada, and Sweden the standards are 8 hour TWAs, as in the U.S. However, in other countries, such as Germany, standards refer to "Maximum Allowable or Maximum Permissible" concentrations (MAC or MPC). These are the highest concentrations which can occur in the workplace at any time except where short term excursions above these levels are allowed.

Occupational health standards used in Ontario generally follow ACGIH guidelines.

The current and proposed standards for aromatic hydrocarbons for Ontario and the U.S. as set by OSHA and ACGIH are listed in Table 14-1.



TABLE 14-1

CURRENT OR PROPOSED OCCUPATIONAL STANDARDS FOR
AROMATIC HYDROCARBONS IN NORTH AMERICA

(All figures are reported as ppm, with equivalent mg/m³ in parentheses)

<u>COMPOUND</u>	<u>ONTARIO</u>		<u>UNITED STATES</u>			<u>ACGIH</u>		<u>REFERENCES</u>
	<u>8 hr TWA</u>	<u>8 hr TWA</u>	<u>OSHA</u> <u>Ceiling</u>	<u>Peak</u>		<u>8 hr TWA</u>	<u>STEL</u>	
Benzene	10(32)	1(3)	5(16) (15 min/8 hrs)	--		10(32)	25(80)	1,2,3
Toluene	100(375)	100(375) ^a	200(750)	--		100(375)	150(56)	1,2,4
Xylene (o-,m-,p-)	100(375)	100(375) ^a	200(870)	--		100(375)	150(655)	1,2,5
Ethylbenzene	100(375)	100(435) ^a	--	--		100(435)	125(545)	1,2,6
Cumene	50(245)	50(245) ^a	--	--		50(245)	75(365)	1,2,6
Styrene	100(420)	100(420) ^a	200(840)	600(2520) (5 min/3 hr)		100(420)	125(525)	1,2,6
Naphthalene	10(50)	10(50)	--	--		10(50)	15(75)	1,2,7

^a Proposed Standard



The U.S. standard for benzene is a new permanent standard, which replaced the old standard of 10 ppm 8 hour TWA, 25 ppm ceiling and 50 ppm peak (not more than 10 min. in any 8 hours) (8). This new standard was reported in the Federal Register of February 10th, 1978 to become effective on March 13th, 1978. However, a federal appeals court in New Orleans has issued a temporary restraining order blocking enforcement of the regulations for at least one month (9). The order was issued in response to a petition filed by the American Petroleum Institute and the National Petroleum Refiners Association. It will be in effect until a hearing, scheduled for April 17th, 1978, is held on the petition.

Table 14-2 lists occupational health standards for aromatic hydrocarbons for Sweden and the German Federal Republic (GFR) (10). It may be noted that the GFR's MPC for benzene is 0 ppm. Most of the other standards listed are similar to the ACGIH, TLV guidelines.



TABLE 14-2

THRESHOLD LIMIT VALUES FOR AROMATIC HYDROCARBONS
IN SWEDEN AND GERMANY

<u>COMPOUND</u>	<u>STANDARD</u>	
	<u>SWEDEN</u> 8 hr TWA, ppm (mg/m ³)	<u>GERMANY</u> MPC, ppm (mg/m ³)
Benzene	10(30)	0(0)
Toluene	100(375)	200(750)
Xylenes	100(435)	200(870)
Ethylbenzene	--	100(435)
Cumene	--	50(245)
Styrene	50(210)	100(420)
Naphthalene	--	10(50)



14.3 AMBIENT AIR STANDARDS

Several countries have regulations governing ambient air concentrations of certain pollutants, such as sulfur dioxide, nitrogen oxides, particulate matter, and total hydrocarbons. Aromatic hydrocarbons are normally considered within the class of total hydrocarbons, and standards have not been set on a compound-by-compound basis. In certain jurisdictions within the U.S. (eg Los Angeles County Air Pollution District, Rule 66), emissions of photochemically reactive compounds are restricted. However, current thinking in the U.S. is to consider all hydrocarbons, except possibly methane, as photochemically reactive, and thus to restrict emissions of all hydrocarbons. This moves away from the principle of compound-specific standards (13).

In contrast, Ontario sets compound-specific half hour point of impingement standards, which include several of the aromatic hydrocarbons of interest. These point of impingement standards are set out in Regulation 15, Schedule 1, of the Revised Regulations of Ontario, under the Ontario Environmental Protection Act. The current version of Rule 15, Schedule 1 dates from June 1st, 1977. Those point of impingement standards dealing with aromatic hydrocarbons of interest here are listed in Table 14-5.

None of these aromatic hydrocarbons are presently listed as part of the Ontario Ambient Air Quality Criteria (12).



TABLE 14-3

HALF-HOUR POINT-OF-IMPINGEMENT STANDARDS
FOR AROMATIC HYDROCARBONS IN ONTARIO

<u>COMPOUND</u>	CONCENTRATION AT POINT OF
	<u>IMPINGEMENT-HALF-HOUR AVERAGE</u> ($\mu\text{g}/\text{m}^3$)
Benzene	10,000
Toluene	2,000
Xylenes	2,300
Ethylbenzene	4,000
Styrene	400



14.4 WATER STANDARDS

No data were found on standards for water quality, either for raw waters, drinking water, or effluents, which specifically deal with any of the aromatic hydrocarbons of interest.

Effluent quality is currently regulated by measurement of such parameters as BOD, COD, TOC, turbidity, fish toxicity, etc.



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